**Effect of Single versus Multiple Hydrogen Bonding on
the Morphology of Self-Assembling Systems:
The Case of Alkyl Carbamates**

by

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in partial fulfilment of the requirements
for the degree of

Master of Science

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ABSTRACT

The effect of alkyl side chain length on the thermal and morphological behaviors of the simple carbamates (N-octadecyl carbamate) of different alkyl side chain lengths with single hydrogen bonding motif has been previously studied by our group. The main focus of the study was to control the morphology of these compounds, which was achieved by homologous blending as well as blending with the other compounds. It is evident from the literature survey that the number of hydrogen bonding sites involved in the self-assembly of the molecules dictates the behavior of the molecules. This has motivated us to study biscarbamates of different alkyl side chain lengths ranging from C₄ to C₁₈ with double hydrogen bonding motifs with respect to thermal and morphological behaviors. The length of the alkyl side chain as well as the method involved in preparing the samples i.e. quenched and slow-cooled has been found to control the morphology of these compounds.

Following an introduction (Chapter 1) and the description of the methods to used for characterization (Chapter 2), Chapter 3 discusses the heat of fusion, percent crystallinity, crystallite size, size of the spherulites, nucleation, the rate of growth of spherulites, and the rate of crystallization of different biscarbamates samples. Chapter 4 focuses on the gelation properties of the biscarbamates such as the critical gelation concentration, gelation time, gelation temperature, and crystallization versus gelation. The hollow nature of the fibers is the most fascinating property of the gels and xerogels. Oriented diffraction patterns from the fibrils of the spherulites (Chapter 3) and the xerogels (Chapter 4) lead

to a model for the growth patterns of the hydrogen bond planes and the molecular orientation in the spherulites and xerogels. The competing role of the hydrogen bond and the van der Waals interactions is also discussed.

A comparative morphological study has also been done between the crystallization and gelation aspects of the hydrogen bond mediated self-assembling systems with single and double hydrogen bonding motifs using simple carbamates of different alkyl side chain lengths as an example. Compared to simple carbamates, biscarbamates show significantly different morphological behavior and these are discussed in detail in Chapter 3 and 4.

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Chapter1

Introduction

1.1 Molecular Self-Assembly

Molecular self-assembly is a spontaneous organization of a group of molecules or segments of similar or different types, into ordered arrangements. These molecules or segments can interact with one another by balanced attractive or repulsive forces. These can be noncovalent (van der Waals forces, coulombic interactions, hydrophobic interactions and hydrogen bonds) interactions. These interactions are generally weak compared to thermal energies^{1,2}. Structural compatibility and complementarity are also key factors in the self-assembly system³. The morphology and thermal behavior of the compounds, which are among the important factors in terms of designing functional materials, change depending on these interactions. This thesis focuses on controlling the morphology of one such class of compounds. In the present work, biscarbamates with different alkyl side chain lengths are used as an example. This work explains how the morphological and thermal behavior change depending on the way the samples were solidified after the melt. It also demonstrates the effect of alkyl side chain length and single versus double hydrogen bonding on the morphology of the self-assembling molecules.

Mobility of the molecules is also important for self-assembly to take place. Therefore, this process is usually conducted in a solution or at an interface so that molecules can attain mobility. The association of molecules could be reversible or irreversible. When the process is reversible the molecules can attain order and the formation of crystals takes place. Whereas, the irreversible association causes disordered arrangement of the molecules resulting in glasses (Figure 1a and b)⁴.

Figure 1.1 Schematic of (a) Disordered glass (b) ordered crystal ⁴.

1.1 Molecular Self-Assembly in Nature

The structures derived from self-assembly are ubiquitous in nature, from the opalescent inner surface of the abalone shell to the internal compartments of the living cell⁵. In the biological system, large molecular complexes and cellular organelles are the result of this magnificent process. The replication of the cell component (cytoplasm and DNA) and assembling into another cell during mitosis (cell division: division of cytoplasm and nucleus) is one of the examples⁶⁻⁸. The tobacco mosaic virus (TMV) is a helical virus particle, 300nm in length, 18 nm in diameter, composed of 2130 identical subunits, each comprising of 158 amino acids⁹⁻¹². A single strand of this viral RNA is 6390 base pairs (bp) in length and the subunits form a helical sheath around this strand (Figure 1.2).

Figure 1.2 (a) TEM image (b) schematic of Tobacco Mosaic Virus¹³.

If the protein coat of TMV was coded by a single, contiguous gene instead of identical subunits, then the RNA required will be 1×10^6 bp in length. Therefore, it proves that the building blocks are responsible for the economy in the use of genetic information. Bacteriophage T4 is another example in this series¹⁴. Studies have also proved that the TMV particles can be readily dissociated into their component parts and then subsequently reassembled accurately in vitro to form totally functional viral particles because of self-assembly^{12,15-17}. In *E. coli* and *Salmonella* the filament is about 200Å in diameter and by self-assembly it can grow up to the length of 15 µm using as many as 30,000 flagellin subunits as building blocks¹⁸. The most well-known and interesting biological paradigm of this process is the formation of the DNA double helix from two complementary oligonucleotides. Self-splicing and self-cleaving RNA, bacteriophage morphogenesis, ribosome assembly, formation of lipid layer, pairing of bases, folding of

some proteins constitute a few examples of self-assembly representations. The stunning diversity of structure and function of biological systems has opened the door for limitless opportunities for the development of self-assembly as a strategy for the fabrication of complex systems⁴.

1.3 Designing of Functional Materials Using Self-Assembly

Biology is replete with examples of self-assembly that has stimulated designs for inanimate systems. By using biomimetic strategy, non-biological molecules can be designed which might offer many opportunities to build systems with new types of functions. Lehn and co-workers have extensively used the self-assembly process for designing new classes of compounds¹⁹. They named one of the classes as deoxynucleoribohelicate, the metal complexes of which mimic some of the features of nucleic acid. Under this category they made the oligonuclear metal complex with a double helical structure²⁰. This structure was found to be similar to the inside-out model of DNA proposed by Pauling and co-worker i.e. it has a positive charge inside the strand and nucleic-acid bases are on the outer spine of the double helix²¹. Therefore, it leads to the possibility that this kind of complex can interact with the negatively charged double-stranded DNA which can result in a composite natural-artificial quadruple helix.

Current research in the self-assembly is focused towards molecular recognition. The addition of recognition with self-assembly leads to more complicated structures. This concept has been used in the synthetic materials, whereby two molecules with matching complementary interactions and shape recognize each other and form a receptor-substrate

supramolecule²². Hydrogen bonds, molecular curvature, and an appropriate guest species are among a few factors that are responsible for this process.

Hydrogen bonding acts as a driving force for many self-assembling molecules, leading to the formation of supramolecules. This only happens when the hydrogen bonding donor and acceptor sides are well aligned and point in the same direction²³. For example, the formation of supramolecular hydrogen bonded nanorods was reported by Reinhoudt and Whitesides^{24,25}. The generation of supramolecules can take place by involving either one or multiple hydrogen bonds. However, the properties of the supramolecules change depending on the number of hydrogen bonds involved during their formation. Designing of supramolecular chain, for instance by using a 1:1 combination of difunctional diamino pyridine and difunctional uracil derivatives, involves three hydrogen bonds^{26,27}. An extensive work has been done by Zimmermann, Meijer and Whitesides in the association process of the molecules leading to heterodimerization involving three hydrogen bonding motifs²⁸⁻³⁰. Lehn et. al., and Singh et. al., have developed the chiral main chain liquid crystals by exploiting the hydrogen bonding between tartaric acid derivatives and bipyridine^{31,32}. These bonds have also been reported as a driving force for the formation of columnar supramolecular polymers. Benzene triamide is one of the widely studied examples in this category. X-ray and IR studies have shown that these molecules arrange themselves in a column via three fold intermolecular hydrogen bonding³³⁻³⁵. The same phenomenon has also been shown by cis-1,3,5-cyclohexane tri carboxamides³⁶.

Recently, efforts have been made to explore quadruple hydrogen bonding motifs which Meijer and his group have synthesized using diaminotriazine and diaminopyrimidines³⁷. Zimmermann and his group have reported dimerization via quadruple hydrogen bonding³⁸. These motifs result in dimerization as well as sort of supra-polymerizations. The supra-polymers are different from conventional polymers. They are reversible in nature and exhibit properties similar to polymers because of the self-association of the corresponding binding motifs. Meijer and coworkers were among the first to synthesize reversible polymers based on this principle by the self-association of a bifunctional 2-ureido-4[1H]-pyrimidione derivatives³⁹.

Owing to the directionality and specificity, hydrogen bonds can control the supramolecular structure of several length scales and anisotropic properties. To achieve functionalities, the principal periodicity is at ≈ 10 to $2000\text{\AA}$ ⁴⁰. This can be attained by using various architectures of block polymers. Depending on the architecture, block length and temperature, different morphologies can be obtained like lamellar, cylindrical, spherical, gyroid, etc^{41,42}. Martin and his group were able to induce assembly of four self-complementary subunits into a pseudo-spherical capsule by exploiting the hydrogen bonding (moderately directional) preferences with the molecular curvature. Then they filled the capsule with the complementary guest molecules leading to the last step of the assembly process⁴³ (Figure 1.3).

Figure 1.3 Schematic representation of a tetrameric assembly⁴³.

Like hydrogen bonding, π stacking has also been found to facilitate the self-assembly of certain class of molecules. Discotic molecules are among them. These molecules have a disc-shaped core generally consisting of a planar aromatic ring and its periphery is usually surrounded by flexible alkyl chains⁴⁴. The strong π interaction between the cores causes these molecules to self-assemble and form supramolecular polymers. Alkoxy substituted triphenylenes are widely studied molecules and also the first among the discotic molecules showing liquid crystalline state^{45,46}. These molecules have small cores and thus the stacking is loose. Phthalocyanines have a larger core compared to substituted triphenylenes and therefore have stronger π stacking⁴⁷. Cyclic *m*-phenylene ethylene oligomers have also been reported to form thermotropic mesophases because of these interactions⁴⁸. The π - π interactions induce polymerization in solution. Alkyl-oxydibenzopyrenes, hexaesters of hexahydroxybenzenes and cyclo hexanes have also shown to form lyotropic mesophase due to these interactions^{49,50}.

The combination of hydrophobicity and hydrophilicity of the molecules have also been found to favor self-assembly⁵¹. When the amphiphilic block copolymers are dissolved in water, which is selective for one-block, aggregation of the molecules takes place, leading to the formation of micelles (Figure 1.4a and b⁵²). Micelles can be of two types either star or crew-cut, depending on the size of the core and corona. The comparative length of the hydrophilic and hydrophobic parts can change the morphology⁵³. For example, when Polystyrene-*b*-poly (acrylic acid) having a relatively longer PAA block, is placed in water, it favors micelles formation. However, when the length of this block is decreased, a transition from micelles to vesicles has been observed⁵⁴. Recently, our group have used the concept of asymmetric structure and have established a very unique example of vesicle formation in a non-aqueous (hexane) medium using perylene end-capped poly(dimethylsiloxane) as self-assembling molecules (Figure 1.4c). They have also demonstrated the effect of the solvents on the morphology of these self-assembling molecules⁵⁵.

Nowadays, micelles are playing a vital role in drug delivery systems. The drug can be loaded in either portion depending on its hydrophobicity or hydrophilicity. Micelles lead to the increase in the bio-availability of the drug and minimize undesirable side effects⁵⁶⁻⁵⁸. There are certain micelles that can actually release the drug at the site of requirement eg poly (L-lactic acid) (PLLA) / poly ethylene glycol (PEG) micelles loaded with adriamycin⁵⁹.

(a)

(b)

(c)

Figure 1.4 (a) Schematic of micelle (b) SEM Micrographs of PS(500)-b-PAA(58) micelles⁵² (c) Trilayer packing model of perylene end-capped PDMS⁵⁵.

Micelles can also be used to make the surface of carbon nanotubes functional. This type of self-assembly can be exploited for the development of new biosensors and bioelectric nanomaterials⁶⁰. The uniform incorporation of nano crystals (NC) in hydrophilic matrices is required for the fabrication of a robust, functional laser^{61,62}. This can be achieved by direct synthesis of water-soluble NC gold micelles and their further assembly with silica into robust, ordered three-dimensional NC array in bulk or in the form of thin films. The intermediate NC micelles are of interest for biolabeling⁶³.

Cyclodextrins (CD) are another example in the series of self-assembling molecules^{64,65}. These are cyclic oligosaccharides with six, seven or eight α -1,4-linked D-glucopyranose rings and termed as α -CD, β -CD, and γ -CD respectively. Their structures are rigid and have a well-defined cavity, which is relatively hydrophobic in nature, and therefore they can easily accept guest molecules⁶⁶⁻⁶⁸. CD can form inclusion complexes with a wide variety of substrates and Bender has exploited this particular property in his seminal work on enzyme mimics^{69,70}. They can also be used as a catalyst for certain reactions and as second sphere ligands in transition metal complexes⁷¹⁻⁷³. Recently, the propensity of CD to form strong complexes in aqueous solution with different types of guests, has shifted the focus of cyclodextrin research as building blocks in manufacturing nanoscale devices through self-assembly. They are widely used in making rotaxanes. Rotaxane is a class of compounds which have a cyclic molecule threaded by a linear molecule and have bulky groups at the ends. In the absence of the bulky groups these molecules are known as pseudorotaxanes (Figure 1.5a and b). These components are linked together mechanically

rather than via a covalent bond. The group of Gibson H.J. and Stoddart J.F have done an extensive study in this area^{74,75}.

Figure 1.5 Schematic representation of (a) rotaxane (b) pseudorotaxane⁷⁶.

Recently, low molecular organo gelators have also become an area of interest. These gels are microheterogeneous phases that self-assemble in a variety of structures ranging from molecular to the micrometer scales. The gelation process can be a result of hydrogen bonding, π interactions, London dispersion forces, charge transfer interactions etc. Gels are very well recognized in our day-to-day life like cosmetics, food, toys, medicines, biomaterials, separation technology and so on⁷⁷⁻⁸².

These are a few examples of self-assembly. It seems that we are at the verge of a materials revolution in which an entirely new class of supermolecules and particles will be designed and fabricated with desired features, including programmable instructions for assembly. These new building blocks will be the atoms and molecules of tomorrow's materials.

1.4 Self-Assembling Biscarbamates

These are self-assembling small molecules. The biscarbamates focused in the thesis have two -NHCOO groups which sandwich six methylene groups (number of spacer groups is constant) and on the other sides they have symmetric alkyl substitution (Figure 1.6). However, the number of carbon atoms in the alkyl substitution varies from one sample to another. Hydrogen bonding and van der Waals forces are responsible for the self-assembly of these molecules. Because of the hydrogen bonding and van der Waals forces, the association process in biscarbamates is similar to that of biological self-assembly. The crystallographic studies have shown that some long chain biscarbamates crystallize in the triclinic system⁸³. Studies on hydrogen bonding and IR spectra of various carbamates have been reported by Furer⁸⁴. This thesis describes the influence of the length of the side group on the morphological features. This is a case of competing or balancing interactions involving hydrogen bonding and van der Waals.

Figure 1.6 Hydrogen bonding in the self-assembly of biscarbamates.

The synthesis and purity of the samples is discussed in the Chapter 2.

1.4.1 Applications of Biscarbamates

Biscarbamates, as a class of compounds, have a long history in terms of scientific studies and technological applications. These are considered model compounds for polyurethanes. Acetylene biscarbamates were investigated by Gaylord in early 1950's. They have also been used as organic intermediates⁸⁵. The decomposition mechanism of polyurethanes has been discussed in terms of that of biscarbamates. They have been used to adjust the viscosity of oil and grease, improve hardness of polyurethane-based adhesive and sealants as anti-inflammatory agents, pesticides, and sequence-specific DNA alkylation agents⁸⁶⁻⁹². These have also been investigated as photosynthetic inhibitors^{93,94}.

Carbamates with alkyl side chains have been investigated for use as ink vehicles for ink-jet printing technologies^{95,96}. These biscarbamates have a melt viscosity of about 8-12 centipoises, melting temperatures of 90-120° C, and crystallize rapidly upon quenching from the melt. These attributes are apt for printing ink technologies. Goodbrand et al have also studied the use of biscarbamates, with alkyl side chains, for use as ink vehicles⁹⁷.

Recently, the studies done in our group on the simple carbamates (N-octadecyl carbamate) with different alkyl side chain length have shown that the technique involved in preparing the sample i.e. slow-cooled or quenched (discussed in Chapter 2) and alkyl side chain length, affect the morphology of these self-assembling molecules. The single hydrogen bonding motif was found to facilitate the self-assembling process. The objective of the study was to control the morphology of these compounds. A wide range

of morphological features were obtained by blending of homologous molecules, blends with other hydrogen bonding molecules such as stearic acid, polyethylene waxes, and commercial clarifiers⁹⁸⁻¹⁰⁰.

It is evident from the literature that the number of hydrogen bonding motifs involved in the self-assembly process has a profound influence on the morphology of the self-assembling molecules. The present work discusses the morphology of the carbamates involving double hydrogen bonding motifs. It also demonstrates the significant differences in the morphological behaviors of biscarbamates with double hydrogen bonding sites, and symmetric substitution of alkyl segment versus N-octadecyl carbamate esters with a single hydrogen bonding motifs and asymmetric alkyl side chain substitution.

1.5 Thesis Objectives

The objectives of the thesis were:

- To synthesize the biscarbamates of different alkyl side chain lengths.
- To investigate the thermal and morphological behavior of biscarbamates.
- To investigate the cooling affect on the morphological behavior of these self-assembling molecules.
- To study the effect of hydrogen bonding and van der Waals forces on the self-assembly of this system.
- To study the growth rate of spherulites of these samples.
- To study the crystallization kinetics of the samples.
- To prepare the low molecular weight organogels (LMOG) of biscarbamates and study the thermal properties of organogels and morphology of the organogels as well as xerogels obtained from the gels.

1.6 References

1. Olenyuk, B.; Whiteford, J.A.; Fechtenkotter, A.; Stang, P.J. *Nature* **1999**, 398, 796.
2. Lehn, J.-M. *Nato ASI Ser. Ser. E* **1996**, 320, 511.
3. Pauling, L. *Nature of the Chemical Bond and the Molecular crystals: An introduction to Modern Structural Chemistry*, 3rd ed.; Cornell University: New York, 1960.
4. Whitesides, G.M.; Bonchevea, M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, 99, 4769.
5. Glotzer, S.C. *Science* **2004**, 306, 419.
6. Shapiro, J. A. *Ann. Rev. Microbiol.* **1998**, 52, 81.
7. Shimoyama, N.; Sugawara, K.; Mizuguchi, T.; Hayakawa, Y.; Sano, M. *Phy. Rev. Lett.* **1996**, 76, 3870.
8. Bonabeau, E.; Dorigo, M.; Theraulaz, G. *Nature* **2000**, 406, 39.
9. Klug, A. *Angew. Chem. Int. Ed.* **1983**, 22, 565.
10. Reisler, E.; Cheung, P.; Borochoy, N. *Biophys. J.* **1986**, 49, 335.
11. Getzoff, E.D.; Tainer, J.A.; Olson, A. J. *Biophys. J.* **1986**, 49, 191.
12. Heck, M.M.S.; Earnshaw, W.C. In *Self- Assembling Architecture*, Varner; J.E., Ed.; Alan R. Liss Inc.; New York, 1988.
13. (a) virus reference: http://www.virology.net/Big_Virology/BVunassignplant.html.
(b) Klug, A.; Caspar, D.L.D. *Adv. Virus Res.* **1960**, 7, 225.
14. Stryer, L. *Biochemistry*, 3rd ed.; W. H. Feeman Comp.; New York, 1988.
15. Fraenkel-Conrat, H.; Williams, R.C. *Proc. Natl. Acad. Sci. USA* **1955**, 41, 690.
16. Lauffer, M. A. *Entropy-Driven Processes in Biology: Polymerization of Tobacco Mosaic Virus Protein and Similar Reactions*, Springer: New York, 1975.

17. Lebeurier, G.; Nicholief, A.; Richards, K.E. *Proc. Natl. Acad. Sci. USA* **1977**, *74*, 149.
18. Yonekura, K.; Maki, S.; Morgan, D.G.; DeRosier, D.J.; Vonderviszt, F.; Imada, K.; Namba, K. *Science* **2000**, *290*, 2148.
19. (a) Lehn, J.-M. *Pure Appl Chem.* **1978**, *50*, 871.
(b) Lehn, J.-M. *Science* **1985**, *227*, 849.
(c) Lehn, J.-M. *Angew. Chem. Int. Ed.* **1988**, *27*, 89.
(d) Lehn, J.-M.; Rigault, A. *Angew. Chem. Int. Ed.* **1988**, *27*, 1095.
20. Koert, U.; Harding, M.M.; Lehn, J.-M. *Nature* **1990**, *346*, 339.
21. Pauling, L.; Corey, R. B. *Nature* **1953**, *171*, 346.
22. Lehn, J.-M. *Supramolecular Chemistry*, VCH: Weinheim, 1995.
23. (a) Brunsveld, L.; Folmer, B.J.B.; Meijer, E.W.; Sijbesma, R.P. *Chem. Rev.* **2001**, *101*, 4071.
(b) Sijbesma, R.P.; Meijer, E.W. *Chem. Commun.* **2003**, *43*, 5.
(c) Beijer, F.H.; Sijbesma, R.P.; Kooijman, H.; Spek, A.L.; Meijer, E.W. *J. Am. Chem. Soc.* **1998**, *120*, 6761.
(d) Beijer, F.H.; Kooijman, H.; Spek, A.L.; Sijbesma, R.P.; Meijer, E.W. *Angew. Chem. Int. Ed.* **1998**, *37*, 75.
24. Klok, H.A.; Joliffe, K.A.; Schauer, C.L.; Prins, L.J.; Spatz, J.P.; Moller, M.; Timmerman, P.; Reinhoudt, D.N. *J. Am. Chem. Soc.* **1999**, *121*, 7154.
25. Choi, I.S.; Li, X.; Simanek, E.E.; Akaba, R.; Whitesides, G.M. *Chem. Mater.* **1999**, *11*, 684.
26. Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990**, *2*, 254.

27. Lehn, J.-M.; *Makromol. Chem. Macromol. Symp.* **1993**, *69*, 1.
28. Zimmerman, S.C.; Corbin, P.S. *Struct. Bonding (Berlin)* **2000**, *96*, 63.
29. Beijer, F.H.; Sijbesma, R.P.; Vekemans, J.A.J.M.; Meijer, E.W.; Kooijman, H.; Spek, A.L. *J. Org. Chem.* **1996**, *61*, 6371.
30. Whitesides, G.M.; Simanek, E.E.; Mathias, J.P.; Seto, C.T.; Chin, D.N.; Mammen, M.; Gordon, D.M. *Acc. Chem. Res.* **1995**, *28*, 37.
31. He, C.; Lee, C.-M.; Griffin, A.C.; Bouteiller, L.; Lacoudre, N.; Boileau, S.; Fouquey, C.; Lehn, J.-M. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sec. A* **1999**, *332*, 251.
32. Singh, A.; Lvov, Y.; Qadri, S.B. *Chem Mater.* **1999**, *11*, 3196
33. Yasuda, Y.; Iishi, E.; Inada, H.; Shirota, Y. *Chem. Lett.* **1996**, *25*, 575.
34. Hanabusa, K.; Koto, C.; Kimura, M.; Shirai, H.; Kakehi, A. *Chem. Lett.* **1997**, *26*, 429.
35. Lightfoot, M.P.; Mair, F.S.; Pritchard, R.G.; Warren, J.E. *Chem. Commun.* **1999**, *19*, 1945.
36. Hanabusa, K.; Kawakami, A.; Kimura, M.; Shirai, H. *Chem. Lett.* **1997**, *26*, 191.
37. Beijer, F.H.; Kooijman, H.; Spek, A.L.; Sijbesma, R.P.; Meijer, E.W. *Angew. Chem. Int. Ed.* **1998**, *37*, 75.
38. Corbin, P.S.; Zimmerman, S.C. *J. Am. Chem. Soc.* **1998**, *120*, 9710.
39. (a) Sijbesma, R.P.; Beijer, F.H.; Brunsveld, L.; Folmer, B.J.B.; Hirschberg, J.B.; Lange, R.F.M.; Lowe, J.K.L.; Meijer, E.W. *Science* **1997**, *278*, 1601.
(b) Sontjes, S.H.M.; Sijbesma, R.P.; van Genderen, M.H.P.; Meijer, E.W. *Macromolecules* **2001**, *34*, 3815.
40. Bates, F. S.; Fredrickson, G.H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.

41. Muthukumar, M.; Ober, C. K.; Thomas, E. L. *Science* **1997**, 277, 1225.
42. Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science* **1997**, 276, 384.
43. Martin, T.; Obst, U.; Rebek, J. *Science* **1998**, 281, 1842.
44. Demus, D., Goodby, J., Gray, G.W., Speiss, H.W., Vill, V. *Handbook of Liquid Crystals*. Wiley-VCH Verlag: Weinheim. 1998; Vol. 2B.
45. Billard, J.; Dubois, J.-C.; Tinh, N.H.; Zann, A. *Nouv. J. Chim.* **1978**, 2, 535.
46. Destrade, C.; Mondon, M.C.; Malthete, J. *Journal de Physique, Colloque* **1979**, 3, 17.
47. van Nostrum, C.F.; Nolte, R.J.M. *Chem. Commun.* **1996**, 21, 2385.
48. Zhang, J.; Moore, J.S. *J. Am. Chem. Soc.* **1994**, 116, 2655.
49. Zamir, S.; Singer, D.; Speilberg, N.; Wachtel, E.J.; Zimmerman, H.; Poupko, R.; Luz., Z. *Liq. Cryst.* **1996**, 21, 39.
50. Usol'tseva, N.; Praefcke, K.; Smirnova, A.; Blunk, D. *Liq. Cryst.* **1999**, 26, 1723.
51. (a) Bruke, S.; Shen, H.; Eisenberg, A. *Macromol. Symp.* **2001**, 175, 273.
- (b) Gao, Z.; Varshney, S. K.; Wong, S.; Eisenberg, A. *Macromolecules* **1994**, 27, 7923.
- (c) Zhang L.; Barlow, R. J.; Eisenberg, A. *Macromolecules* **1995**, 28, 6055.
- (d) Zhang, L.; Eisenberg, A. *J. Am. Chem. Soc.* **1996**, 118, 3168.
- (e) Yu, K.; Eisenberg, A. *Macromolecules* **1998**, 31, 3509.
52. Zhang, L.; Eisenberg, A. *Polym. Adv. Technol.* **1988**, 9, 677.
53. Yu, K.; Eisenberg, A. *Macromolecules.* **1996**, 29, 6359.
54. Zhang, L.; Eisenberg, A. *Science* **1995**, 268, 1728.

55. Yao, D.; Bender, T.P.; Gerroir, P.J.; Sundararajan, P.R. *Macromolecules*. **2005**, *38*, 6972.
56. Fan, H.; Yang, K.; Boye, D.M.; Sigmon, T.; Malloy, K.J.; Xu, H.; Lopez, G.P.; Brinker, C.J. *Science* **2004**, *304*, 567.
57. Desai, M.P.; Labhasetwar, V.; Amidon, G.L.; Levy, R. *J. Pharm. Res.* **1996**, *13*, 1838.
58. Francis, M.F.; Cristea, M.; Winnik, F.M. *Pure Appl. Chem.* **2004**, *76*, 1321.
59. Jeong, Y.; Cheon, J.B.; Akaike, T.; Cho, C.S. *J. Contrl. Rel.* **1998**, *51*, 169.
60. Dieckmann, G.R.; Dalton, A.B.; Johnson, P.A.; Razal, J.; Chen J.; Giordano, G.M.; Munoz, E.; Musselman, I.H.; Baughman, R.H.; Draper, R.K. *J. Am. Chem. Soc.* **2003**, *125*, 1770.
61. Richard, C.; Balavoine, F.; Schultz, P.; Ebbesen, T.W.; Mioskowski, C. *Science* **2003**, *300*, 775.
62. Sundar, V.C.; Eisler, H. J.; Bawndi, M. G. *Adv. Mater.* **2002**, *14*, 739.
63. Petruska, M.A.; Malko, A.V.; Voyles, P.M.; Klimov, V.J. *Adv. Mater.* **2003**, *15*, 610.
64. Saenger, W. *Angew. Chem. Int. Ed.* **1980**, *19*, 344.
65. Stoddart, J. F. *Carbohydrate Res.* **1989**, *192*, 12.
66. Bergeron, R. J. *Inclusion Comp.* **1984**, *3*, 391.
67. Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*, Springer: New York, 1978.
68. Szejtli, J. *Inclusion Comp.* **1984**, *3*, 331.
69. Cramer, F. *Angew. Chem.* **1952**, *64*, 136.
70. Griffiths, D. W.; Bender, M. L. *Adv. Catal.* **1973**, *23*, 209.
71. Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66.

72. (a) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.
(b) Breslow, R. *Science* **1982**, *218*, 532.
(c) Breslow, R. *Chem. Br.* **1983**, *19*, 126.
(d). Breslow, R. *Acc. Chem. Res.* **1995**, *28*, 146.
73. Colquhoun, H.M.; Stoddart, J.F.; Williams, D.J. *Angew. Chem. Int. Ed.* **1986**, *25*, 487.
74. Gibson, H.W.; Bheda, M.C.; Engen, P.T. *Progress in Polymer Science* **1994**, *19*, 843.
75. (a) Ashton, P. R.; Becher, J.; Fyfe, M. C. T.; Nielsen, M. B.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2001**, *57*, 947.
(b) Balzani, V.; Credi, A; Marchioni, F.; Stoddart, J.F. *Chem. Commun.* **2001**, *18*, 1860.
(c) Chiu, S.H.; Rowan, S.J.; Cantrill, S.J.; Glink, P.T.; Garrell, R.L.; Stoddart, J. F. *Organic Lett.* **2000**, *2*, 3631.
76. Sundararajan, P.R. In *Physical properties of Polymers Handbook*, Mark J.E., Ed.; American Institute of Physics Press, New York, 1996; Chap1.
77. Lee, E.S.; Na, K.; Rae, X.H. *J. Contl. Rel.* **2003**, *91*, 103.
78. Terech, P.; Weiss, R.G. *Chem. Rev.* **1997**, *97*, 3133.
79. Liangde, L.T.; Cocker, T.M.; Bachman, R.E.; Weiss, R.G. *Langmuir* **2000**, *16*, 20.
80. Abdallah, D.J.; Weiss, R.G. *Adv. Mater.* **2000**, *12*, 1237.
81. George, M.; Weiss, R.G. *Langmuir* **2002**, *18*, 7124.
82. Loose, M.D.; Feringa, B.L.; van Esch, J.H. *Eur. J. Org. Chem* **2005**, *2005*, 3615
83. Alimova, L.L.; Atovmyan, E.G.; Filipenko, O.S. *Kristallografiya.* **1987**, *32*, 97.
84. (a). Furer, V.L. *J. Mol Struc.* **1998**, *449*, 53.
(b) Furer, V.L. *J. Mol Struc.* **1999**, *513*, 1.

- (c) Furer, V.L. *J. Mol Struc.***1999**, 476, 215.
- (d) Furer, V.L. *J. Mol Struc.***2000**, 520, 117.
85. Gaylord, N.G. *J. Org. Chem.* **1955**, 20, 546.
86. Saka, K.; Noda, K. Jpn. Kokai Tokkyo Koho JP 62 179 584 (1987). Chem. Abstr. 108, 39820r.
87. Tanaka, K.; Kano, Y.; Yoshida, K. Jpn. Kokai Tokyo Koho JP 63 248 894 (1988). *Chem Abstr.* 110, 79137w.
88. Kinoshita, H.; Sekiya, M.; Mishima, M., Eur. Pat. Appl. EP 274 756 (1988). Chem Abstr. 109, 233979k.
89. Steichele, K. Pat. Belg. 882,922 (1980). Chem Abstr. 94, 66768d.
90. Giudicelli, R.; Najer, H.; Chabrier, P.; Joannic, M. *Annales Pharma. Franca.* **1956**, 14, 376.
91. D'Silva, T. D. J. U. S. Patent 4400389 (1983).
92. Atwell, G. J.; Fan, J.Y.; Tan, K.; Denny, W.A. *J Med. Sci.* **1998**, 24, 4744.
93. Chueca, A.; Baron, M.; Lopez Gorge, J. *Unidad Bioquim. Veg., Estac. Exp. Zaidin, Granada, Spain. Photosynth., Proc. Int. Congr.*, 5th ed.; Balaban Int. Sci. Serv., Philadelphia, Pa, 1981.
94. Chueca, A.; Baron, M.; Lopez-George, J. *Revista Espanola de Fisiologia* **1982**, 38, 315.
95. Jpn. Kokai Tokyo Koho JP 58 201 758 (1983). . Chem Abstr. 100, 174289z.
96. Tanaka, T.; Yoshitomi, T.; Hanada Y.; Ohashi, M.; Takeda, Y. Jpn. Kokai Tokkyo Koho JP 6 290 289(1987). Chem Abstr. 107, 20896b.

97. Goodbrand, B.; Boils, D.; Sundararajan, P.R.; Wong, R.; Malhotra, S. U.S. Patent 6, 187, 082, (2001).
98. Moniruzzaman, M.; Goodbrand, B.; Sundararajan, P.R. *J. Phys. Chem. B* **2003**, *107*, 8416.
99. Moniruzzaman, M.; Sundararajan, P.R. *Pure Appl. Chem.* **2004**, *76*, 1353.
100. Moniruzzaman, M.; Sundararajan, P.R. *J. Phys. Chem. B* **2005**, *109*, 1192.

Chapter 2

Materials and Methods

2.1 Introduction

The morphological and thermal behavior of materials changes during the process of crystallization and gelation. These changes can be assessed by using a combination of experimental techniques such as differential scanning calorimetry (DSC), X-ray diffraction (XRD), hot-stage optical microscopy (OM) and scanning electron microscopy (SEM). This chapter describes these techniques, used to study the morphological and thermal behavior of different members of the biscarbamates class of compounds. It also discusses the synthesis and purification of these compounds. In this study, the purity of the compounds was checked by IR and ^1H NMR spectroscopy. The terms used in the morphology have also been described in brief. The spectra for each compound have been placed in the Appendix A, B.

2.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry is a technique that is used very often for quantitative studies of thermal transitions in polymers, metals, ceramics, composites and organic materials. The sample and an inert reference are heated, usually in a nitrogen atmosphere, and thermal transitions in the sample are detected and measured. An average-temperature circuit measures and controls the temperature of the sample and sample holders to conform to a predetermined time-temperature program. At the same time, a temperature-difference circuit compares the temperatures of the sample and reference holder and proportions power to the heater in each holder so that the temperature remains equal (Figure 2.1). When the sample undergoes a thermal transition, the power to the two heaters is adjusted to maintain their temperatures. The temperature is plotted along one

axis of a x-y recorder and a signal proportional to the power difference is plotted along the second axis of the recorder.

Figure 2.1 Schematic representation of Differential Scanning Calorimetry measuring cells.

The area under the resulting curve is a direct measure of the heat of transition. The applications of DSC include determination of melting temperature (T_m), the crystallization temperature (T_c), glass transition temperatures (T_g) and the specific heat capacity (C_p) of the materials ^{1, 2}.

In this study, thermal analysis was performed using a DuPont 2010 differential scanning calorimeter at a heating rate of 10 °C / minute. The instrument was calibrated for temperature and energy with indium and tin reference samples. DSC traces were recorded in a nitrogen atmosphere. The uncertainty was $\pm 1^\circ\text{C}$ for the melting point and $\pm 2 \text{ J/g}$ for the heat of fusion.

Samples were prepared in two ways for DSC analysis. The ‘slow cooled’ samples were prepared by melting a small amount of material (7-8 mg) in an aluminum pan at a temperature of 20 °C higher than its melting point. It was held isothermally for about 15 minutes to remove any morphological history. It was then cooled slowly to room temperature at the rate of 10 °C /minute. The second set of samples, termed as ‘quenched’ samples were prepared by following the same procedure except that they were quenched immediately from the melt.

The crystallization kinetics was studied using a TA Instruments Q100 MDSC. After heating the samples to a temperature 20 °C higher than their melting point in the DSC, they were cooled to their crystallization temperature and the heat of fusion was measured at intervals of 0.6sec. The crystallinity was determined by integrating the isothermal heat flow curve with respect to time. The degree of crystallization (α) can be represented as:

$$\alpha = \frac{\Delta H_t}{\Delta H_{\infty}} = \frac{\int_0^t \frac{dQ}{dt} dt}{\int_0^{\infty} \frac{dQ}{dt} dt} \quad (2.1)$$

ΔH_t = partial area between the DSC curve and the time axis at time t.

ΔH_{∞} = total area under the peak and corresponds to the overall heat of crystallization.

The $t_{1/2}$ was calculated by plotting a graph between the degree of crystallization (α) and time (t).

2.3 Optical Microscopy (OM)

The optical microscope with polarized light in the transmission mode was used to study the optical characteristics of the biscarbamates samples. In general the spherulitic structure of materials is not visible to the naked eye, so it has to be studied using cross-polarized light microscopy. In a cross-polarized setting the polarizer and analyzer are placed in such a way that their orientation axes are perpendicular to each other.

The spherulites can be defined as birefringent areas showing a dark extinction pattern in the shape of a Maltese cross of which one arm is aligned with the vibration direction of the polarizer and the other is aligned with the vibration direction of the analyzer. The molecules have dipole and when polarized light is passed through the molecules, all the molecules transmit the light except the ones which are perpendicular to the orientation axis of the polarized light. The molecules that cannot transmit the light appear as a black band. Similarly, the molecules that are perpendicular to the orientation axis of the analyzer also cannot transmit light and form a dark band. These two dark bands perpendicular to each other give rise to a Maltese cross. Therefore, when a sample is studied under crossed polars, only those molecules perpendicular to neither the polarizer nor the analyzer are visible- these are at $\approx 45^\circ$ to each polaroid.

The sign of the spherulite birefringence depends on the orientation of the optic axes of the crystalline domain with respect to the polarization direction of the incident light. The sign of the spherulite can be determined by using a sensitive tint plate (λ plate) that can add to the path difference of the spherulite or subtract from it, depending on whether the

birefringent units in the spherulite are oriented parallel to the plate or perpendicular to it. This means that one pair of quadrants of a spherulite will be raised up the scale of colors and the other will be lowered. Therefore, with spherulites showing only first-order white, which is normal in a thin section, one pair will be raised to blue and the other lowered to orange. The housing of the λ plate has an arrow showing the polarization direction. If the quadrants of the spherulite parallel to the arrow appear orange and the other quadrants appear blue, the spherulites are called negative spherulites. On the other hand, in the case of positive spherulites the quadrants perpendicular to the arrow of the plate are orange in color and the parallel quadrants are blue in color. Depending on the thickness of the sample the colors may vary ³. Figure 2.2 shows the appearance of the positive and negative spherulite under optical microscope.

Figure 2.2 Schematic presentation of (a) positive (b) negative spherulite and (c) tint (λ) plate.

A Zesis Axioplan polarised optical microscope (OM) was used for recording the optical micrographs of biscarbamates. Both quenched and slow cooled samples were prepared in the same way as for the DSC studies except that instead of aluminum pans, glass slides were used here. For kinetic studies of spherulite growth, a Linkam hot stage LTS 350 was used, with a Linkam TMS 94 controller. The samples were heated to a temperature 20 °C higher than their melting point, at the rate of 5 °C /minute and held there isothermally for about 10 min. They were then cooled at the rate of 2 °C /minute up to 5 °C above the crystallization temperature (T_c) and then at 0.1 °C /minute up to the T_c . Northern Eclipse (version 6.0) image processing software was used to capture the images and calculate the spherulite size.

2.4 Scanning Electron Microscopy (SEM)

The scanning electron microscope uses a high-energy electron beam obtained from the emission of tungsten filament, to form images. This beam is passed through a series of lenses and scanning coils, which place a small spot of electrons on the specimen. These electrons penetrate the surface and produce secondary electrons. Secondary electrons get liberated from the specimen surface and the detector collects these electrons and sends the signals to an amplifier and the image is recorded. The SEM can produce three-dimensional images of high resolution, which means that closely spaced features can be examined at a high magnification ^{4,5,6}. SEM provides useful information on surface topology with a resolution of about 100Å⁻¹. The combination of large depth of focus, greater resolution, and higher magnification makes the SEM a very useful instrument in research areas today.

SEM images were obtained using a JEOL JSM-6400 scanning electron microscope. Xerogels were mounted on double-sided carbon tape placed on an aluminum slide. The samples were coated with 60: 40 Au / Pd using a sputter coater (Hummer VII model by Anatech Ltd.). They were then placed inside the SEM under vacuum. The images were captured at room temperature. The accelerating voltage of the beam was 15 kV.

Images of gels were recorded using the SEM under cryo stage. Gels were mounted on flat brass specimen holders. Then the samples were inserted in a cryo-transfer chamber. Here the samples were frozen in a nitrogen gas atmosphere. Then the cryo-transfer chamber was evacuated and the samples were placed in the SEM. The samples were heated to $-90\text{ }^{\circ}\text{C}$ to remove any traces of frost in the vacuum of SEM and again the temperature was cooled to $-150\text{ }^{\circ}\text{C}$. Then the samples were again brought to the cryo-transfer chamber and an aluminum coating was evaporated on the surface. Finally, the samples were placed back in the SEM, which was held at $-150\text{ }^{\circ}\text{C}$ and the images were recorded at an accelerating voltage of 7kV.

2.5 X-ray Diffraction (XRD)

A crystal is a complex, although orderly, arrangement of atoms. All atoms in the path of an X-ray beam scatter X-rays simultaneously. In general, the scattered waves interfere with and destroy one another, but in certain specific directions they combine to form new wave fronts. This cooperative scattering is known as diffraction. The directions of the possible diffraction depend only on the size and shape of the unit cell. Therefore, the X-ray diffraction method is a powerful tool for investigating orderly arrangement of

atoms or molecules through the interaction of electromagnetic radiation to give interference effects with structures comparable in size to the wavelength of radiation^{7,8}.

A single crystal is required in order to get complete information of the molecular ordering in a crystalline or semi-crystalline material. The diffraction patterns at all possible angles are recorded by rotating the crystal about an axis perpendicular to the incident beam. During the unavailability of single crystal, a powder X-ray diffractometer can be used. Valuable information can be extracted by using this instrument, such as interplanar distances between atomic planes (d spacing), crystallite size and percent crystallinity. In powder X-ray diffraction, the reflections are obtained from several microcrystals with random orientation.

The basic equation of X-ray diffraction is the Bragg formula:

$$2d \sin\theta = n\lambda \quad (2.2)$$

Where d, is the distance between the atomic planes, θ the angle of incidence of the x-ray beam on the atomic planes, λ the wavelength of x-ray radiation and n (1,2,---, n) is the order of reflections.

Figure 2.3 Reflection from a crystal structure.

The Figure 2.3 shows a plane of beam of parallel x-rays penetrating a stack of planes of spacing d , at a glancing angle of incidence θ . Each plane must be pictured as reflecting a fraction of the incident beam ⁹.

Rearrangement of Bragg's equation gives the d -spacing as:

$$d = \frac{\lambda}{2\sin\theta} \quad (2.3)$$

The above equation (3) shows that when the distance between the two planes in the lattice is large, the scattering angle (2θ) has to be small to produce a diffraction pattern. The diffraction obtained at angles smaller than 2° ($d \approx 50\text{\AA}$) is called Small Angle X-ray Scattering (SAXS). The diffraction obtained at all larger angles, theoretically extending up to 180° is called Wide Angle X-ray Diffraction (WAXD). WAXD provides information about the spatial arrangement of the atoms, whereas, SAXS provides the information about domain arrangement (e.g. long spacing).

In the present work, a Philips automated powder diffractometer (PW 1710) was used for X-ray diffraction studies with Ni-filtered Cu K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$). Diffraction data were recorded in the range of $2^{\circ} \leq 2\theta \leq 50^{\circ}$, using the software MDI Datascan 3.2 (Materials Data Inc., Livermore CA). The possible presence of texture was checked by taking additional diffractograms with the sample turned in the plane of measurement by 90° . Figure 2.4 shows a schematic of the Bragg diffraction with the diffractometer¹⁰. The results were analyzed using the MDI Jade 5.0 XRD pattern processing software. Samples were prepared in the same way as for the DSC except that in this case glass holders were used to hold the samples. X-ray scans were recorded at room temperature.

Figure 2.4 Schematic of the Bragg diffraction with the powder X-ray diffractometer used for the present study (from Alexander¹⁰). Here, S₁, S₂ and S₃ are the divergence slit, receiving slit and scatter slit respectively; angular range (α) = $1-4^{\circ}$.

2.5.1 Percent Crystallinity

Percent crystallinity can be measured by using powder x-ray diffractometer. It is the ratio of crystalline peaks to the sum of the crystalline and amorphous intensities and can be calculated using the formula:

$$\text{Percent crystallinity} = \frac{I_{\text{crystalline}}}{I_{\text{crystalline}} + I_{\text{amorphous}}} \times 100 \quad (2.4)$$

Here $I_{\text{crystalline}}$ is the area under the crystalline peaks and $I_{\text{crystalline}}$ and $I_{\text{amorphous}}$ is the total area (Figure 2.5).

Figure 2.5 Schematic for calculating percent crystallinity.

The Figure 2.5 shows the schematic diffractogram of a semi-crystalline sample. First the amorphous area under the peaks is marked by using the Fit- Background option of the MDI Jade 5.0 XRD software and then the percent crystallinity is calculated.

2.5.2 Crystallite Size

Crystallite size is the growth of a crystalline region along a specific lattice direction. It can be calculated by measuring the broadening of a particular peak in a diffraction pattern. The crystallite size is inversely related to the full width at half maximum (FWHM) of the particular peak (Figure 2.6). If the peak is narrower, the crystallite size will be larger.

Figure 2.6 The schematic of full width at half-maximum peak (FWHM).

The crystallite size L , corresponding to a particular reflection was calculated by using the Scherrer Equation¹⁰:

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (2.5)$$

Here λ is wavelength of the X-ray, θ is half of the scattering angle, β is the half width of the peak on the 2θ scale in radians; $K=0.9$.

The biscarbamate samples showed significant X-ray reflections at $2\theta < 5^\circ$. The diffraction patterns obtained at $2\theta < 5^\circ$ from the powder x-ray diffractometer are not well resolved due to the overlapping with the background. Therefore, patterns were also recorded on film, using a Statton type flat film camera (William Warhus Co., Wilmington, DE), using Cu K_α radiation, with sample to film distance of 10 cm and 17 cm. A schematic of a Statton –type Warhus flat film camera is shown in Figure 2.7.

Figure 2.7 Schematic of a Statton-type Warhus flat film camera.

Film X-ray is also a very good source of obtaining information regarding the crystalline or amorphous nature of the material. Since the recording is two-dimensional, any crystalline and amorphous orientation in the specimen can also be detected. Although the measurements of the intensities is not straight forward as in a diffractometer, photographic technique can be used to measure the intensities and also the degree of orientation. The typical diffraction recorded on film for amorphous (halo),

semicrystalline randomly oriented (rings) and oriented (arcs) samples are shown in Figure 2.8. Also shown is a pattern that is obtained with single crystals.

Figures 2.8 Diffraction from (a) amorphous (b) semi crystalline but unoriented (c) semi-crystalline with orientation (d) single crystals.

2. 6 FTIR Spectroscopy

Infrared (IR) spectroscopy is an extremely powerful analytical technique for both qualitative (fingerprinting of compounds; recognition of specific chemical bonds, or groups; gross structural features) and quantitative (measurements of reaction rates, determination of thermodynamic data, process and control) analysis. The underlying basis of applied IR spectroscopy is the fact that practically all-organic compounds possess selective absorption at certain frequencies in the IR portion of the electromagnetic spectrum ^{11,12}. Organic applications of infrared spectroscopy are almost entirely concerned with the range of 650- 4000 cm^{-1} . The region of frequencies below 650 cm^{-1} is called the far infrared whereas the region above 4000 cm^{-1} is known as near infrared. The information regarding the functional group present in a molecule is obtained from the region between 1400- 4000 cm^{-1} . The region from 600-1400 cm^{-1} is known as fingerprint region because the pattern of absorption in this region is unique to any particular compound ^{13,14}. A plot of transmission or absorption values versus frequency or wavelength units constitutes an IR spectrum, which is a characteristic of the sample being studied.

The absorption of infrared is a quantized process. The bonds between the atoms in a molecule vibrate with certain energy. When the molecules are exposed to the IR radiation, the frequencies of the radiation, which match the natural vibrational frequencies of the molecules, get absorbed. All the bonds cannot absorb IR radiation. To absorb radiation, bonds should have dipole moments. A change in a dipole moment takes place with a change in the position of the centers of positive and negative charges due to

the atomic motions ^{15,16}. This changing electrical dipole moment of the bond then interacts with the changing electromagnetic field of the incoming radiation. The matching frequency is absorbed and this absorbed energy increases the amplitude of the vibrational motion of the bonds and the molecules are excited to a higher energy state. This gives rise to the absorption bands appearing on the spectrogram. Basically there are two different modes of vibrations in a molecule which are infrared active i.e. stretching and bending. Further, stretching vibrations can be symmetric or asymmetric while bending can be classified as scissoring, wagging, rocking, and twisting.

Michelson M129 BOMEN Fourier Transform Infrared (FTIR) spectrometer was used for the present studies. The experiments were run at ambient conditions. Data were collected using BOMEN GRAMS / 386 software. The samples were sandwiched between two NaCl discs and were melted at a temperature 20 °C higher than their melting points and then either slow cooled or quenched. In certain cases, the FTIR spectra of the samples were recorded in the form of transparent KBr pellets. A background FTIR spectra was taken for each experiment with an identical sample holder.

2.7 Synthesis and Characterization of the Biscarbamates

The synthesis of the biscarbamates was performed as described by Goodbrand et al.¹⁷ Biscarbamates were synthesized by reactions of 1,6, diisocyanato hexane (0.1 mol) with appropriate alcohols (0.2mol), 1-butanol, 1-hexanol, 1-octanol, 1-dodecanol, 1-hexadecanol and 1-octadecanol (Scheme 1) separately in the presence of a catalyst 1,4-diazabicyclo [2,2,2] octane (DABCO). The reaction was carried out in toluene

(200 ml), at 80-85 °C for 5 hours except for 1-octadecanol (8-9 hours). For example 1,6-hexanediyl-bis-dihexadecyl carbamate was prepared by taking 16.82gm (0.01 mole) of 1,6, diisocyanato hexane in a 500ml round bottom flask equipped with a reflux condenser and a nitrogen purge. Then 48.4gm (0.2 mole) of hexadecanol along with 200ml of toluene and 20mg 1,4-diazabicyclo [2,2,2] octane were added to the same flask and the mixture was refluxed for 5hrs. The solution was cooled and 1,6-hexanediyl-bis-dihexadecyl carbamate was obtained after filtration. All these reagents were purchased from Aldrich.

Reaction products obtained after filtration were purified by dissolving them in a small amount of toluene at 60 °C for recrystallization and then the solution was cooled slowly. This procedure was repeated twice in order to remove any impurity or unreacted reagents (1,6 diisocyanato hexane and respective alcohols). Infrared and ¹HNMR spectroscopies were used to confirm their purity.

Scheme 2.1 Preparation of biscarbamates.

The names of the synthesized compounds are listed in Table 2.1, and for convenience each of them has been given a name C_x, where x denotes the number of carbon atoms in the alkyl side chain. These sample IDs (C_x) will be used through out this thesis.

TABLE 2.1 Biscarbamates synthesized from reaction of an appropriate alcohol with 1,6, diisocyanato hexane.

Parent molecule	Product ID	Product Name 1,6-hexanediyl- bis-	Molecular Formula	T _m °C (from DSC)
1-butanol	C ₄	di butyl carbamate	H ₉ C ₄ COONH (CH ₂) ₆ NHCOOC ₄ H ₉	91.3
1-hexanol	C ₆	di hexyl carbamate	H ₁₃ C ₆ COONH (CH ₂) ₆ NHCOOC ₆ H ₁₃	97.1
1-octanol	C ₈	di octyl carbamate	H ₁₇ C ₈ COONH (CH ₂) ₆ NHCOOC ₈ H ₁₇	106.7
1-dodecanol	C ₁₂	di dodecyl carbamate	H ₂₅ C ₁₂ COONH (CH ₂) ₆ NHCOOC ₁₂ H ₂₅	114.9
1-hexadecanol	C ₁₆	di hexadecyl carbamate	H ₃₃ C ₁₆ COONH (CH ₂) ₆ NHCOOC ₁₆ H ₃₃	117.8
1-octadecanol	C ₁₈	di octadecyl carbamate	H ₃₇ C ₁₈ COONH (CH ₂) ₆ NHCOOC ₁₈ H ₃₇	120.4

2.7.1 FTIR Spectra of the Biscarbamates

The samples were prepared by mixing 5mg of the biscarbamate with dried KBr and were ground into a fine powder. High pressure (1471.00 MPA) was then applied by means of a hydraulic press to coalesce the samples into a transparent or semitransparent disk. The prepared sample was mounted in the cell, which was aligned with the infrared beam of the spectrometer. The FTIR spectra of all the biscarbamates show a strong carbonyl stretching vibration (amide I band) at $\approx 1682\text{ cm}^{-1}$. The band due to C=O out-of-plane vibrations was observed at 782 cm^{-1} , which is a characteristic band as it is used as an internal standard in the IR spectra of polyurethanes¹⁸. The amide II band, which is due to N-H bending appears at $1537\text{-}1539\text{ cm}^{-1}$ where as N-H stretching frequencies¹⁹ are recorded at $3319\text{-}3324\text{ cm}^{-1}$. Figure 2.9 represents the FTIR spectra of the C₁₆ sample and the stretching frequencies of some of the bands observed in its spectra are listed in Table 2.2.

Figure 2.9 FTIR spectrum of C₁₆.

Table 2.2 Stretching Frequencies of the IR bands of the biscarbamates.

Frequency (cm ⁻¹)	Assignment
3319	N-H stretching
2952	CH ₃ asymmetrical stretching
2916	CH ₂ asymmetrical stretching
2849	CH ₂ symmetrical stretching
1682	C=O stretching vibrations
1472	CH ₃ bending
1264	C-O stretching
1144	C-N stretching
649	C-N deformation
1539	CHN gp vibration
782	C=O out-of-plane vibration
718	(CH ₂) _n -in -phase rocking ²⁰

2.7.2 ^1H NMR Spectra of the Biscarbamates

The ^1H NMR spectra were taken in deuterated chloroform using a 400 MHz spectrometer (Bruker). Tetramethylsilane (CH_3) $_4\text{Si}$ was used for internal calibration. Figure 2.10 represents the ^1H NMR spectra of C_{16} . For convenience this spectra has been divided into two parts. In the ^1H NMR spectrum the CH_3 protons show a triplet around δ 0.87 ppm, N- CH_2 absorption at around δ 3.18 ppm splits into a quartet by coupling with the N-H and neighboring CH_2 proton. The N-H proton shows a broad signal around δ 4.63 ppm. The signal is affected by the magnetic and electric properties of ^{14}N nucleus in such a way as to make it appear as a broad signal²¹. The $-\text{O}-\text{CH}_2$ protons show a triplet around δ 4.02 ppm. The remaining CH_2 protons show a multiplet around δ 1.25 – 1.60 ppm.

Figure 2.10 . ^1H NMR Spectrum of C_{16} .

2.8 References

1. Stevens, M.P. *Polymer Chemistry an Introduction*, 3rd ed.; Oxford University Press: New York, 1999; Chap. 5.
2. Laye, P.G. In *Principles of Thermal analysis and Calorimetry*, Haines, P.J., Ed.; The Royal Society of Chemistry: Cambridge, 2002; Chap. 3.
3. Savile, B.P. In *Applied Polymer Light Microscopy*, Hemsley, D.A., Ed.; Elsevier Science Publishers Ltd.: New York, 1989; Chap. 4.
4. Curson, A.D. In *Applied Polymer Light Microscopy*, Hemsley, D.A., Ed.; Elsevier Science Publishers Ltd.: New York, 1989; Chap. 1.
5. Thornton, P.R. *Scanning Electron Microscopy, Applications to Materials and Device Science*, Chapman and Hall Ltd.: London, 1968; Chap. 2.
6. Temple Black, J. In *Principles and Techniques of Scanning Electron Microscopy*, Hayat, M.A., Ed.; Van Nostrand Reinhold Comp.: New York, 1974; Chap. 1.
7. Billmeyer, F.W. *Textbook of Polymer science*, 3rd ed.; Wiley-Interscience: New York, 1984; p 238.
8. Wunderlich, B. *Macromolecular Physics, Crystals, Structure, Morphology and Defects*, Academic Press: New York, 1973; Vol. 1.
9. Nuffield, E.W. *X-ray Diffraction Methods*, John Wiley and Sons, Inc.: New York, 1966; Chap. 3.
10. Alexander, L.E. *X-ray Diffraction methods in Polymer Science*, Wiley-Interscience: New York, 1969.

11. Pavia, D.L.; Lampman, G.M.; Kris, G.S. *Introduction to spectroscopy*, 2nd ed.; W.B. Saunders Comp.: Philadelphia, 2001; Chap. 2.
12. Bowling Barnes, R.; Gore, R.C.; Liddel, U.; Williams, V.Z.; *Infrared Spectroscopy Industrial Applications and Bibliography*, Reinhold Publishing Corp.: New York, 1944.
13. Kalsi, P.S. *Spectroscopy of Organic Compounds*, 4th ed.; New Age International Ltd.: New Delhi, 2000; p 60.
14. Kemp, W. *Organic spectroscopy*, 3rd ed.; Macmillan Education Ltd.: London, 1991.
15. Herzberg, G. *Molecular spectra and molecular spectrum*, 2nd ed.; Van Nostrand Reinhold Comp.: New York, 1950.
16. Steinfield, J.I. *Molecules and radiations, an introduction to Molecular spectroscopy*, The MIT Press: Cambridge, 1985.
17. Goodbrand, B.; Boils, D.; Sundararajan, P.R.; Wong, R., US Patent 6,414,051, 2002.
18. Furer, V.L. *J. Mol. Struct.* **2000**, 520, 117.
19. Socrates, G. *Infrared characteristics group frequencies*, Wiley-Interscience: New York, 1980; Chap. 10.
20. Nin-Vien, D.; Colthup, N.B.; Fateley, W.G.; Grasselli, J.G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press Inc.: Boston, 1991; p 14.
21. Kalsi, P. *Spectroscopy of Organic Compounds*, 4th ed.; New Age International Ltd.: New Delhi, 2000; p 255.

Chapter 3

Morphology and Thermal Behavior of Biscarbamates

3.1 Introduction

In this chapter, the morphology and thermal behavior of carbamates with double hydrogen bonding motifs, with symmetric alkyl substitution on either side of the hydrogen bonding groups is discussed. The spherulitic morphology and crystallization depends on the alkyl chain length. It is interesting that there exists an alkyl chain length with which the spherulite size, and the rates of spherulite growth and crystallization show a maximum. We illustrate the differences between the morphologies rendered by single and double hydrogen bonding motifs.

In a series of papers¹⁻³, it has been discussed (i) the effect of alkyl chain length on the crystallization and morphology characteristics of these simple carbamates, (ii) effect of nucleating agents and clarifiers on controlling the spherulite size and crystallinity of the solid, and (iii) the role of the alkyl chain length and solvent on their capability to form organogels.

The difference in the sequence, and the symmetry of the alkyl side chains on either side of the hydrogen bonding motif as illustrated below for a C₈ side chain, would no doubt affect the morphology, and crystallization characteristics.

Both are hydrogen-bonding systems. The biscarbamate has two hydrogen-bonding sites and symmetric disposition of the alkyl chains. In this chapter, we describe the effect of the alkyl side chain on the crystallization behavior and morphology of a series of biscarbamates, and compare it with the simple carbamates with a single hydrogen-bonding moiety. The effect of the alkyl side chain length on the growth rate of spherulites is also discussed. As far as we know, this is the first time the crystallization kinetics of these materials has been reported.

3.2 Results and Discussion

3.2.1 Thermal Behavior

The crystallization and morphology of simple carbamates, with alkyl side chains of different lengths were discussed in previous publications^{5,6,23}. As noted above, these have a single hydrogen-bonding motif and the alkyl side chains on either side of this motif were asymmetric. We describe here the behavior of biscarbamates, with double hydrogen bonding motif, and symmetric length of the alkyl side chains.

The biscarbamates studied here showed sharp melting points and only one phase transition from solid to the melt. These results, along with the absence of any polymorphic transitions prior to melting indicate their purity. The melting temperatures (T_m) along with the crystallization temperatures (T_c) for both the slow cooled and quenched samples are shown in Figure 3.1, as a function of the number of carbon atoms in the alkyl side chain. The T_m increases sharply from C_4 to C_8 and then moderately with a further increase in the length of the alkyl side chain. No difference was noted in the

melting points of slow cooled and quenched samples. The T_m 's corresponding to the simple carbamates studied before are also shown in this figure, for comparison. For each of the side chain lengths, the T_m for the biscarbamate is higher than that of the simple carbamate. This can be attributed to both the symmetry of the side chains on either side of the hydrogen bonding moiety, as well as the possibility of two hydrogen bonds for each molecule of the biscarbamate. It is seen from Table 3.1 and Figure 3.1 that the

Figure 3.1 Melting (T_m) and crystallization temperatures (T_c) of slow cooled and quenched samples for biscarbamates with different alkyl chain lengths. The T_m 's of the simple carbamates are also shown.

Table 3.1 Molecular lengths and melting temperatures of the biscarbamates with different alkyl side chain lengths.

Parent molecule	Sample ID	Molecular Formula	Molecular length*, Å	T _m °C (from DSC)
1-butanol	C ₄	H ₉ C ₄ COONH (CH ₂) ₆ NHCOOC ₄ H ₉	23.01	91.3
1-hexanol	C ₆	H ₁₃ C ₆ COONH (CH ₂) ₆ NHCOOC ₆ H ₁₃	28.12	97.1
1-octanol	C ₈	H ₁₇ C ₈ COONH (CH ₂) ₆ NHCOOC ₈ H ₁₇	33.27	106.6
1-dodecanol	C ₁₂	H ₂₅ C ₁₂ COONH (CH ₂) ₆ NHCOOC ₁₂ H ₂₅	43.82	114.9
1-hexadecanol	C ₁₆	H ₃₃ C ₁₆ COONH (CH ₂) ₆ NHCOOC ₁₆ H ₃₃	53.52	117.8
1-octadecanol	C ₁₈	H ₃₇ C ₁₈ COONH (CH ₂) ₆ NHCOOC ₁₈ H ₃₇	59.06	120.4

*Length of the molecules calculated using Hyper Chem Pro 6 molecular visualization and simulation software (Hypercube Inc.).

increment in T_m decreases with an increase in the alkyl chain length. There is an increase of 9.5 °C from C₆ to C₈, but only 2.7 °C between C₁₆ and C₁₈. Studies of McKierman et al⁴ on aliphatic polyurethanes showed that with an increase in the length of the aliphatic sequence, the T_m of the polymer decreased and approached that of polyethylene, due to the reduced contribution of the hydrogen bond energy, relative to the van der Waals interaction. A similar trend is observed in the present case of the biscarbamates as well. The heat of fusion increases with the alkyl side chain length (Figure 3.2) with a sharp increase from C₄ to C₈. Similar to the trend in T_m, the rate of increase of heat fusion decreases with the alkyl chain length. As expected, the heats of fusion of slow cooled samples were found to be higher than those of the quenched samples.

Figure 3.2 The variation of the heat of fusion with alkyl side chain length of biscarbamates.

3.2.2 IR Analysis

No noticeable differences were observed in the IR spectra of slow cooled and the quenched samples. Both showed IR absorptions corresponding to the hydrogen bonded N-H and C=O groups at $\cong 3324$ and 1682 cm^{-1} respectively. This indicates that the extent of hydrogen bonding is independent of whether the sample was slow cooled or quenched. However, it is seen from Table 3.2 that the peak intensity of H-bonded N-H and C=O bands increase slightly from C₄ to C₈ and then it decreases with the further increase in the alkyl side chain length. This Table also shows that the peak width at half maximum for

hydrogen bonded N-H increases for C₄ to C₆ and marked decrease thereafter. Such reduction in the half width was related to the increase in crystalline order in the case of a simple polyurethane⁵. The absorption frequencies of CH₂ anti-symmetric and symmetric vibrations decrease from C₄ to C₁₈. These will be discussed later with respect to the spherulite size and crystallization kinetics.

Table 3.2 IR Spectral Results for the N-H and C=O groups for the biscarbamates with different alkyl chain lengths.

Sample Description	H-bonded N-H			H-bonded C=O		
	Peak Position (cm ⁻¹)	Intensity	Peak width at half maximum	Peak Position (cm ⁻¹)	Intensity	Peak width at half maximum
C ₄	3324	59.3	92.8	1682	52.8	70.7
C ₆	3322	60.0	102.1	1681	52.7	68.6
C ₈	3321	66.3	74.6	1682	61.3	67.6
C ₁₂	3321	45.2	73.8	1682	49.2	60.6
C ₁₆	3319	39.2	61.3	1682	46.3	60.1
C ₁₈	3319	35.5	62.2	1682	40.0	54.7

3.2.3 X-Ray Diffraction and Structural Features

The X-ray powder diffractometer traces for the quenched samples of the biscarbamates are shown in Figure 3.3. It is seen that all of them exhibit the most intense peak at $2\theta < 5^\circ$. Similar to the case of simple carbamates, a number of reflections are seen in the range $18 < 2\theta < 26^\circ$. The d spacings corresponding to the quenched and slow cooled samples are listed in Tables 3.3 and 3.4, respectively, along with the relative intensities.

The large d -spacings that could not be recorded with the diffractometer were collected on films, and the intensities of these are denoted as strong (s), medium (m)

Figure 3.3 X-ray diffraction patterns of biscarbamates, with various chain lengths.

and weak (w). A previous study has shown that the compound C₁₂ crystallizes in the triclinic crystal system⁶. Due to the symmetry of the side chains on either side of the hydrogen bonding motif, the C₁₂ biscarbamate shows a centre of symmetry in the crystal structure. It is not our objective here to determine the crystal structure. However, some comments can be made on the powder diffraction data. It is seen from Table 3.3 that the largest d spacing recorded for each biscarbamate generally increases from 23.43 Å for C₄ to 43.69 Å for C₁₈. Although the largest d spacing is 33.6 Å for C₆, C₈ and C₁₂, this reflection is most intense only for the latter. It is also noted that the d spacing of the most intense reflection increases from 19.19 to 43.69 Å as the alkyl chain length increases from C₄ to C₁₈. Figure 3.4a shows the linear increase in the

Table 3.3 Interplanar spacings d (Å) and Relative Intensities (%) obtained from X-ray diffraction patterns of quenched samples.

C_4		C_6		C_8		C_{12}		C_{16}		C_{18}	
d	I	d	I	d	I	d	I	d	I	d	I
								39.77	100 (s)	43.69	100 (s)
		33.67	2.3	33.64	4.1	33.69	100 (s)				
		27.24	70.5			27.50	24.8			27.67	45.1
				26.91	100 (s)						
23.43	w										
		22.8	100 (s)								
20.89	m										
19.19	100 (s)										
		17.01	w								
						16.47	w				
								14.91	w	14.86	w
		13.84	w	13.42	3.3			13.47	w/m		
				13.24	m/w						
		11.47	16.7					11.25	w	11.15	4.4
10.57	m							10.13	3.6		
9.98	w			9.85	w	9.44	w				
9.58	46.70										
		8.49	w	8.87	w	8.41	6.9	8.18	w		
		7.6	1.4	7.82	w			7.53	w	7.46	6.0
				7.39	w						
6.31	2.40	6.43	w	6.7	7.7	6.72	w	6.76	3.6		
		6.10	w								
		5.11	w			5.18	w			5.14	w
		4.95	w	4.90	w	4.95	w	4.99	w	4.98	w
4.62	16.03	4.61	28.4	4.65	31.1	4.69	45.1	4.64	62.3	4.66	77.1
4.26	40.30	4.31	9.9	4.40	22.4	4.49	38.6	4.51	77.6	4.53	98.2
		4.18	58.4	4.22	19.7	4.29	22.6	4.35	21.0	4.39	11.6
				4.12	77.1	4.19	16.1	4.12	23.3	4.19	21.6
								4.03	w	4.04	16.6
		3.99	27.4	3.97	w						
		3.80	20.2	3.82	58.7	3.81	69.3	3.89	37.9	3.89	49.6
										3.81	61.2
3.78	59.00	3.72	10.7					3.79	56.8		
								3.58	64.1		
				3.67	14.6	3.61	31.7			3.60	87.7
		3.42	7.5	3.48	19.8	3.55	23.1				
3.31	5.40										
		3.29	3.2								
						2.44	3.7	2.42	6.6		
								2.39	3.7		

Table 3.4 Interplanar spacings d (Å) and Relative Intensities (%) of slow cooled samples obtained from X-ray diffraction patterns.

C ₄		C ₆		C ₈		C ₁₂		C ₁₆		C ₁₈	
d	I	d	I	d	I	d	I	d	I	d	I
								40.48	100 (s)	43.69	100 (S)
						33.69	100 (s)				
				30.34	m						
		28.34	m								
				26.11	100 (s)						
		23.23	100 (s)								
21.06	m										
18.94	100(s)										
		16.65	w								
										14.86	1.80
				13.18	7.30			13.43	w		
		12.72	w								
		11.59	15.2							11.09	3.400
10.47	m							10.15	10.10		
9.50	59.70					7.90	m				
		7.67	w			7.77	w	7.39	w	7.39	4.60
		7.1	w								
		6.33	w	6.63	13.50	6.30	w	6.78	9.70		
								5.80	w		
		5.76	w			5.73	w				
										5.55	w
						5.20	w	5.24	w		
5.16	w	5.6	w	5.08	2.0	5.11	w				
						4.9	w				
		4.77	w			4.71	2.6	4.74	1.3		
4.62	19.50	4.64	5.30	4.66	w	4.64	w	4.67	w	4.66	43
										4.53	58
		4.41	w			4.4	m				
4.39	w	4.34	m					4.3	w	4.39	9.30
4.25	52.70	4.21	12.0			4.2	m	4.21	w		
				4.18	3.20					4.19	10.0
		4.04	m			4.04	w	4.05	7.0	4.04	14.20
		3.92	w								
		3.82	57.60	3.80	75.30	3.80	53.80	3.80	48.0	3.80	41.90
3.77	45										
						3.52	34.50	3.57	32.80	3.59	50.30
		3.42	6.40	3.45	22.20

Figure 3.4 The variation of (a) the molecular length (l), and the d -spacing with the highest relative intensity with the alkyl chain length of biscarbamates (b) the crystallite size (L) corresponding to the 3.8 and 4.6 Å reflections (c) The relative intensities of the 4.6 Å (quenched) and 3.8 Å reflections (slow cooled) samples respectively.

calculated length of the molecules and the d spacing of the most intense reflection as a function of the chain length. Table 3.3 also shows that a reflection with a d -spacing of 4.6 Å ($2\theta = 19.29^\circ$) is common to all the samples, and that its intensity increases almost linearly from C_4 to C_{18} as shown in Figure 3.4c. To account for this reflection, a simple molecular modelling was performed (using the Hyperchem software) by placing four

molecules of C₁₂ biscarbamate in proximity and minimizing the energy. The resulting molecular packing is shown in Figure 3.5. The distance between the alkyl chains in this model is 4.6 Å. This d spacing thus corresponds to the plane of hydrogen bonding, the intensity of which increases with the alkyl chain length (Figure 3.4c). This reflection was either weak or absent in the case of simple carbamates. The reflection with a spacing of 3.8 Å ($2\theta = 23.4^\circ$) is also common for the biscarbamates, with a fairly strong intensity. In the previous study on the simple carbamates, this reflection was identified with the hydrogen-bonding plane¹. However, it appears that with the biscarbamates, which have double hydrogen bonding for each molecule, the distance between the alkyl chains increases to 4.6 Å. The increase in its intensity with the length of the alkyl chain indicates that the side chain packing is enhanced. For this set of molecules, we thus identify the 4.6Å reflection with the hydrogen-bonding plane and the 3.8Å reflection with the distance between these planes. The inter-sheet distance was 3.8Å in the crystal structure of C₁₂ also⁶. It is known that the distance between the chains in the polyethylene crystal structure is about 4.5Å. A reflection with this spacing was also observed in the case of aliphatic polyurethanes, and was attributed to the distance between the hydrogen-bonded chains⁴. The inter-sheet distance between such hydrogen-bonded chains was associated with a reflection at 3.7Å.

The crystallite size corresponding to the 3.8 and 4.6Å reflections ($2\theta = 23.4$ and 19.3° respectively) for the quenched samples are shown in Figure 4b. The crystallite size for $d = 4.6\text{Å}$ increases sharply from C₄ to C₆ with no significant increase thereafter. However, for $d = 3.8\text{Å}$, the crystallite size increases sharply from C₄ to C₈, and

Figure 3.1 Packing model of bis-carbamate with C₁₂ side chain: (a) hydrogen bonding plane (b) stacking of hydrogen bonding planes (c) schematic of meridional and equatorial reflections in the X-ray diffraction and (d) the sample area used for (c) [see also Figure 3.12].

decreases significantly with a further increase in the side chain length. This behavior will be correlated to the spherulitic growth rates later.

Table 3. 4 lists some of the reflections for the slow cooled samples. The 4.6 and 3.8 Å reflections are common to all the biscarbamates. But the relative intensity recorded for the d spacing of 3.8 Å increases from C₄ to C₈ and then it decreases significantly (Table 3.4 and Figure 3.4c) while the intensities for the d-spacing 4.6 Å don't show any trend. This was traced to the molecular orientation (see below) of the lamellae in the spherulites in the samples prepared by slow cooling. Similar to the heat of fusion (Figure 3.2), the X-ray crystallinity increases with an increase in alkyl side chain length. This is not shown here due to uncertainties in the intensities arising from the molecular orientation of the samples

3.2.4 Spherulitic Morphology

Cross-polarized optical micrographs for the quenched and slow cooled samples are shown in Figure 3.6. As expected, the spherulites from slow cooled samples are larger than those obtained by quenching. This is similar to the case of simple carbamates. There is a striking feature in this figure: with both quenching and slow cooling, the spherulite size increases up to C₈, and then there is a significant decrease. This departs from the behavior of simple carbamates, with which there was no significant difference in spherulite size up to an alkyl chain length of C₁₂, beyond which the size increased significantly. The quenched and slow cooled samples of C₄ did not show any proper spherulites. However, very small birefringent units were observed in the

Figure 3.1 Optical micrographs of quenched (left) and slow cooled (right) samples of biscarbamates with different alkyl chain lengths.

quenched sample, whereas dendrites were seen with the slow cooled samples. The quenched samples of C_6 show fibrillar spherulites, with high birefringence. The slow cooled samples of the same material showed large spherulites with weak birefringence. The optical micrographs of both quenched and slow cooled samples of the compounds C_8 to C_{18} showed the presence of spherulites with negative birefringence. This indicates that similar to the case of polyethylene, the alkyl chains are disposed along the tangential direction of the spherulite.

Figure 3.7 shows the variation of spherulite size for quenched and slow cooled samples, as a function of the number of carbon atoms in the alkyl side chain. The spherulite sizes of the slow cooled samples are several times larger than those of the quenched counterparts. As noted above, in both the cases spherulite size increases from C₆ to C₈ and then decreases. The formation of large spherulites is a result of fewer nuclei. The decrease in the size of spherulite with the increase in the length of the alkyl side chain beyond C₈ can be attributed to the increase in van der Waals attraction. This increased association between the alkyl chains could contribute to increased nucleation density.

The increase in the van der Waals interactions (i.e., attractive contribution to the energy) with an increase in the alkyl side chain length is reflected in the frequencies of the CH₂ symmetric (ν_s) and asymmetric (ν_{as}) absorption bands. Figure 3.8 shows the variation of ν_s and ν_{as} CH₂ stretching vibration modes for the different alkyl chain lengths. The ν_s and ν_{as} decrease with an increase in the length of the alkyl side chain. For C₄, ν_{as} and ν_s are observed at 2935 cm⁻¹ and 2863 cm⁻¹ respectively. They shift to 2917 cm⁻¹ and 2849 cm⁻¹ for C₁₈. The shift to lower wave numbers from C₄ to C₁₈ is indicative of strong organization of the alkyl groups via van der Waals interactions⁷. It was noted above that the half width of the peaks of H-bonded N-H and C=O peaks was also found to increase from C₄ to C₈ and then decrease. The reduction in the half width is indicative of the increase in order²⁷.

When the alkyl side chain is short (C₄ to C₈) the hydrogen bonding interaction dominates over the van der Waals interactions. As the side chain length increases (C₁₂-

Figure 3.7 Radii of the spherulites of (a) quenched (b) slow cooled samples with different alkyl side chain lengths.

C₁₈) the van der Waals attraction becomes more significant, in addition to the hydrogen bonding interaction. This leads to the enhanced packing of the alkyl side chains.

The variation of spherulite size seen here with the length of the alkyl side chain, is very different from the trend that was observed with the simple carbamates studied before (Figure 2 of Ref 1). In the latter, the spherulite size varied very little with the side chain length up to C₁₂, and the increase was significant for C₁₈. Note that in that case, the (single) hydrogen-bonding motif was asymmetrically flanked by the alkyl chains, until the length reached C₁₈. However, in the present case, the alkyl chains are symmetrically positioned on either side of the double hydrogen-bonding motif. Thus, the alkyl chain dispositions contribute to the differences in the spherulitic morphology seen between the two cases.

Figure 3.8 Wavenumber (cm⁻¹) of asymmetric and symmetric CH₂ stretching vibrations for various alkyl side chain lengths.

3.2.5 Spherulitic Growth Rates

In order to further investigate the influence of the alkyl side chains on the spherulitic crystallization, isothermal kinetic studies were performed using the Linkam hot stage. As an example, Figure 3.9 shows a series of micrographs recorded at different times, for C_{12} . This sample showed a T_m of 115°C and a crystallization temperature of 102.8°C in the DSC. For the isothermal crystallization kinetic study, the sample was heated to 135°C , the temperature was reduced to 102.5°C , and the micrographs were recorded at different times to follow the spherulite growth. It is seen that after one second, the fibrillar growth is dumb-bell shaped. Extensive branching of the fibrils occurs with time. It appears that the entire growth is dominated by sequential branching of the lamellae. Similar experiments were performed with the other biscarbamates, by crystallizing the samples about 0.5°C below the T_c observed in the DSC. The variation of the size of the spherulites with time is shown in Figure 3.10a for the biscarbamates with C_6 , C_8 , C_{12} , C_{16} and C_{18} side chains. It is seen that the growth is complete (due to impinging) within 10 sec in the case of C_8 , whereas it takes about 29 sec for C_{16} and C_{18} to complete the growth. It is also seen in this figure that the plots for C_8 , and C_{12} do not extrapolate to a spherulite size of zero at time = 0 sec. This is due to the extremely fast growth of the spherulite in less than a second. The growth rate plotted in Figure 10b shows that the maximum growth rate occurs with C_8 , and it decreases significantly with the longer side chains. This accords with the maximum spherulite size seen with C_8 in the case of quenched and slow cooled samples (Figure 3.7). The significant

Figure 3.9 Optical micrographs recorded during the isothermal crystallization of the C_{12} biscarbamtes, with time. The times (sec) are shown in the figures.

Figure 3.10 (a) Growth of spherulitic radii with time for different biscarbamate samples.

(b) Rate of growth of spherulite radii versus number of carbon atoms in the alkyl side chain.

contribution from the van der Waals interaction between the alkyl side chains leads to such dependence on the side chain length.

3.2.6 Rate of Crystallization

In addition to the rate of growth of the spherulites during isothermal crystallization, the rate of crystallization is also influenced by the length of the alkyl side chain. Figure 3.11 shows the fractional heat of crystallization (α) as a function of time, for C_8 and C_{12} , as the sample was held at the crystallization temperature in the DSC. As noted with the spherulite growth, the rate of crystallization is faster with C_8 than C_{12} . The $t_{1/2}$ values are 0.13 and 0.66 minutes for C_8 and C_{12} respectively.

Figure 3.11 Fractional heat of fusion versus time for C_8 and C_{12} samples.

3.2.7 Orientation and a Model for Growth

It was noted before that the X-ray diffractometer traces of slow cooled samples indicated orientation. The fibrillar growth of the spherulites shown in Figure 3.9 confirms this observation. In some of the cases, due to their large size, the spherulites could be seen with the naked eye. In order to gain some insight into the growth pattern of the spherulites, X-ray diffraction patterns were recorded on film using the flat-film camera. To this end, the sample was positioned on the beam collimator using the optical microscope, so as to locate the fibrillar part in the path of the X-ray beam. Diffraction patterns of this type have been reported only in a few publications⁸, using micro-diffraction or other sophisticated means. Here we used a simple flat film camera. Figures 12a and 12b show the oriented X-ray patterns obtained in this manner for C₆ and C₁₂. The part of the spherulite that was in the X-ray beam is also shown. The d-spacings of the reflections are marked. It is seen that in both cases, the 4.6 Å reflection is on the equatorial direction and the 3.8 Å reflection appears on the meridian. A schematic of these reflections, with respect to the packing of C₁₂ molecules is illustrated in Figure 3.5. The radial direction of the spherulite corresponds to the growth direction of the hydrogen bonding plane, as evidenced by the 4.6 Å equatorial reflection. In addition to the reflection at 3.8 Å, those with larger spacing (e.g., 11.5 Å for C₆ and 7.9 Å for C₁₂) are also seen along the meridian. As the schematic in Figure 3.5 shows, the axis of the individual molecule (i.e., the direction of the alkyl chain) is along the tangential direction of the spherulites, indicating the origin of negative birefringence.

Figure 3.12 X-ray diffractograms of (a) C_6 and (b) C_{12} isothermally crystallized samples, from the oriented fibrillar part (c) of the spherulite (d) schematic of X-ray diffractions recorded on a flat film.

3.3 Conclusions

Molecules that self assemble via hydrogen bond show significant differences in the morphology depending on the number of hydrogen bonding motifs in the molecule, and the symmetry of the side groups. In the case of simple carbamates, the size of the spherulites do not increase significantly until the alkyl chain reaches a length that would impart symmetry on either side of the hydrogen bonding group. With the biscarbamates studied here, such symmetry is inherent in the molecule, and a gradual increase in spherulite size is seen. However, even if the disposition of the alkyl side chains were symmetric, the size of the spherulites, both with quenching and slow cooling, do not increase with the alkyl chain length, but shows a maximum with C₈. We rationalize this behavior on the basis of the nucleation rate that is controlled by the relative contributions to the hydrogen bond and van der Waals energy in the packing of two molecules. As the alkyl side chain length increases, the van der Waals attraction between these segments increases. This is supported by the shift of the CH₂ frequencies to lower wavelengths, with increasing length of the alkyl chain. As mentioned above, McKierman et al⁴ noted that in the case of aliphatic polyurethanes, “dilution” of the hydrogen bond contribution relative to van der Waals interactions occurs with an increase in the length of the alkyl segment. Although we are not dealing with a polymer in the present work, but a small molecule model, a similar dilution or compensation occurs beyond an alkyl chain length of C₈.

In the previous study on simple carbamates, kinetic measurements could not be made (with the facilities available to us) due to the fast crystallization. The current study

shows that the rates of both spherulite growth and crystallization depend on the side chain length, showing the maximum with an alkyl chain of C₈.

Due to the large size of the spherulites, we were able to record oriented X-ray diffraction patterns that show the hydrogen bonding between the molecules to be along the radial direction of the spherulites. In this case however, there was no difference in the direction of growth between the molecules with short and long alkyl chains (e.g., between C₆ and C₁₂).

The results presented here demonstrate that single and multiple hydrogen bonding motifs lead to different morphologies, and that the symmetry and length of the side chains play an important role. We believe that studies of this type would provide insight into the factors that govern the morphology and enable control of the morphology for the functional context.

3. 4 References

1. Moniruzzaman, M.; Goodbrand, B.; Sundararajan, P. R. *J. Phys. Chem. B* **2003**, *107*, 8416.
2. Moniruzzaman, M.; Sundararajan, P. R. *Langmuir*, **2005**, *21*, 3802.
3. Moniruzzaman, M.; Sundararajan, P. R. *J. Phys. Chem. Part B* **2005**, *109*, 1192.
4. McKierman, R. L.; Heintz, A. M.; Hsu, S. L.; Gido, S. P.; Penelle, J. *Polym. Mater. Sci. Eng.* **2001**, *84*, 416.
5. Coleman, M. M.; Lee, K. H.; Skrovanek, D. J.; Painter, P. C. *Macromolecules* **1986**, *19*, 2149.
6. Alimova, L.L.; Atovmyan, E.G.; Filipenko, O.S. *Kristallografiya*. **1987**, *32*, 97
7. Suzuki, M.; Nakajima, Y.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Langmuir*, **2003**, *19*, 8622.
8. Ishikawa, S.; Kurita, T.; Suzuki, E. *J. Polym. Sci.* **1963**, Part B, *1*, 127; Tanaka, T.; Fujita, M.; Takeuchi, A.; Suzuki, Y.; Uesugi, K.; Doi, Y.; Iwata, T. *Polymer* **2005**, *46*, 5673.

Chapter 4

Gels of Biscarbamates

4.1 INTRODUCTION

Gelation of liquids by small quantities of covalently cross-linked polymers (molecular weight above 3000), proteins and inorganic substances like silica or clay have been known for several centuries¹⁻³. Recently, small molecules (molecular weight < 3000) have entered in this competition and established a new class of gels known as low molecular weight organic gelators (LMOGs), which are still in their age of infancy. Certain cholesterol and anthracene derivatives⁴, fatty acid derivatives^{5,6}, carbohydrates⁷, peptide derivatives⁸, amino acid derivatives^{9,10}, porphyrins and phthalocyanines¹¹, n-alkanes¹², bis-urea^{13,14}, condensed aromatic rings¹⁵, etc. are some of the extensively studied examples of the organo gelators. These gelating agents of enormous structural diversity have a common trait i.e. self-assembling property. Gelator molecules self-assemble by highly specific non-covalent interactions forming fibrous structures. These fibrous structures form a three-dimensional network, which is capable of holding the solvent in its interstitial spaces primarily by surface tension. Therefore, self-complementary and unidirectional intermolecular interactions can be considered a prerequisite for gelation ability¹⁶. The intermolecular interactions between the organo gelator molecule can be hydrogen bonding¹⁷⁻²⁰, London dispersion forces, electrostatic attractions, and π stacking¹².

In the recent years LMOGs got the attention of researchers primarily because of their completely reversible nature. They can be easily transformed into solution or back to the gel structure by heating and cooling the samples above and below the sol-gel transition temperature respectively. Secondly, a low concentration is sufficient for gel formation,

and the network filaments (length up to few micrometers) are formed by well-ordered array of molecules. Various shapes of the filaments eg. tapes, rods, fibers, sheets and cylinders have been known so far.

Detailed studies on their interesting properties and architectural elegance have resulted in enormous applications of gels. The reversible nature of gels can be used to make matrices for certain products where they can be easily removed after depositing the required components on demand eg. ink, paints, cosmetics etc. They are widely accepted in the controlled release of drugs, fragrance, photonic materials, catalyst²¹, pH sensitive light and metal responsive²², crystal²³ and fuel engineering²⁴ etc.

An innovative and environmentally friendly method of designing reversible gels was introduced in the late 90s. In this method an organic gelling agent is dissolved in supercritical CO₂ at high temperature and pressure and when the solution is cooled, gel formation occurs²⁵. The basic requirement for the design of the novel gelling agent and what are the phenomenon involved in gelation is studied by various groups^{16,26,27}.

In most of the cases hydrogen bonding has been found as a sole driving force behind gelation and certain groups like amide, carbamate, amino acid derivatives and urea are some of its examples. Jadzyn and coworkers²⁸ have broadened the spectrum of knowledge related to gelation with respect to hydrogen bonding. They found that even a very small concentration of urea has a tendency to form aggregates by intermolecular hydrogen bonding. Later on, different approaches were tried to enforce more non-covalent interactions in urea by using a combination of different groups. Among several

approaches, the addition of a second urea group was found to be highly successful. It has also been noticed that by increasing the number of spacers between two urea groups, the molecule becomes more susceptible to gelation²⁹. Moreover, the previous study done from our laboratory on simple carbamates of different alkyl side chain length has shown that certain members of the series undergo gel formation³⁰. In all these cases the key factor for gelation is hydrogen bonding. But on the contrary, some compounds (5 α -Cholestan-3 β -yl *N*-(2-Aryl)carbamate) and their derivatives that form gel have a urethane group but still do not show strong evidence of hydrogen bonding³¹. The simple alkyl chain has been found to undergo gelation due to London dispersion forces and it is not required for them to be sandwiched between different groups. Studies have also shown that with the increase in the length of the alkyl chains the probability of gelation increases¹².

Extensive studies have been done to establish a relationship between the nature of the gels and the structure of the gelators. The gelation ability and the properties of gels not only depend on the structure of the gelating agent but also on the nature and properties of the solvent. Unfortunately so far, the structural requirement and the relationship between gel and solvent properties for gelation is not very well understood except in a few cases. As a result most of the time organo gelators have been discovered by serendipity^{16,30}.

As is evident from the plethora of literature, molecules of self-assembling nature and favoring hydrogen bonding have a strong inclination towards gelation. This has prompted our interest to explore the gelation ability of biscarbamates.

For the present work we have used the same solvent (benzonitrile) and gel preparation technique as used for the simple carbamates gels to study how single versus double hydrogen bonding motifs effect the morphology of the gels. *This chapter discusses*

(a) The effect of the procedure involved in the gelation process i.e. slow cooled or quenched on critical gelator concentration, gelation versus crystallization, and the morphology of the xerogels and gels.

(b) The effect of alkyl side chain length on:

(i) critical gelator concentration, gelation versus crystallization, and the morphological changes in xegels and gels of quenched and slow cooled.

(ii) gelation time and sol-gel transition temperature of slow cooled samples.

(c) The effect of concentration on gelation time, sol-gel transition temperature, crystallization versus gelation of the slow cooled samples.

(d) Hollow nature of the fibers.

(e) The effect of different shear rates on the morphology of the slow cooled samples.

(f) Hydrogen bonding versus van der Waals forces.

(g) Orientation of the fibers.

4.2 Preparation of the Gels and Xerogels

Gels were prepared in vials (15 x 45 mm) with caps on them to avoid evaporation of the gelating agent (Benzonitrile). Weighed amounts of biscarbamates of different alkyl side chain lengths were dissolved in the requisite amount of benzonitrile at a temperature ranging from 95-110°C, resulting in biscarbamates / benzonitrile clear solution. From these solutions two categories of gels were made- quenched (1) and slow cooled (2). The samples of category (1) were prepared by quenching the clear solution in an ice bath whereas when the same solutions were slowly cooled to room temperature by turning the hot plate off, samples of category (2) were formed. Then the vials were turned upside down to check the gelation. If the samples were not visually separated and did not flow perceptibly they were considered as gels. All the gels were opaque. These gels were dried at room temperature for few weeks and then kept under vacuum for few days. As a result the removal of benzonitrile and the formation of xerogels took place.

4.3 Results and Discussion

4.3.1 Critical Gelator Concentration

The critical gelator concentration (CGC; i.e. the lowest concentration of gelator required to gel a liquid) for the slow cooled and quenched samples was investigated for all the members of the family. The decrease in the CGC values was recorded with the increase in the alkyl side chain length. CGCs have not been found to be affected by the technique involved in the preparation of the samples i.e. quenched or slow cooled (Figure 4.1a and 1b respectively) except for the C₈. Compared to simple carbamates, biscarbamates require more concentration to gelate the solvent³⁰. The critical gelator concentration for

the slow cooled and quenched C₄ member has been found to be 1.2M. Because of the high CGC we didn't consider this member for the further studies.

(a)

(b)

Figure 4.1 Critical gelator concentration (a) quenched and (b) slow cooled gels.

4.3.2 Critical Gelation Time

Since the length of the alkyl side chain affects the CGCs, the next step was to explore whether these chain lengths affect the gelation time G_t (time required for gelation, in minutes). Therefore, the kinetics study of the different alkyl side chain length of the slow cooled gel with the same concentration (0.08M) was undertaken. It was found that with the increase in the alkyl side chain length the value of G_t decreases (Figure 4.2).

Figure 4.2 Alkyl chain length versus Gelation time and temperature.

Therefore, it can be concluded that the samples with the longer alkyl side chain form a gel in less time compared to samples of shorter alkyl side chain. It is interesting to note that the bis-carbamates of longer alkyl side chain length (C_{16} and C_{18}) were able to form

gels whereas their simple carbamates counterparts favored only crystallization³⁰. The reason behind it could be the higher percent crystallinity and heat of fusion of simple carbamates. The previous study done on the simple carbamates has shown that the heat of fusion and percent crystallinity of the samples ranging from C₄ to C₁₂ is almost the same whereas for the longer alkyl side chain members (C₁₆ and C₁₈) they shoot up. However, the heat of fusion of biscarbamates increases sharply from C₄ to C₈ and then it increases gradually (Chapter 3). The simple carbamates require less molar concentration to form gel compared to the bis-carbamates counterparts.

4.3.3 Thermal Behavior of 0.08M Gels

The thermotropic behavior i.e. the sol-gel transition temperatures, exothermic and endothermic transitions were measured with the DSC. The gelation temperature for the slow cooled sample (0.08M) versus alkyl side chain length was recorded and presented in Figure 4.2. An increase in gelation temperature was observed with the increase in the alkyl side chain length. Similarly, an increase in the gel to sol temperature was also recorded with the increasing alkyl side chain length. It was found to be 39.5 °C for C₆ whereas for the C₁₈ it was recorded as 90.6 °C. This shows that the C₁₈ gels stay stable at the higher temperature compared to the C₆ gels. Therefore, it can be concluded that the thermal stability of the slow cooled gels increase from C₆ to C₁₈. The quenched gels also follow the same pattern. A similar trend has also been observed in the case of n-alkanes¹². The sol to gel temperature was found to be 8-10 °C lower than the gel to sol temperature in every case.

In both cases (quenched and slow cooled gels) all the members have shown the thermoreversible sol-gel transition temperature along with the endothermic and exothermic peaks of the crystals-melt transitions of the biscarbamates (Figure 4.3). This shows that the crystallization was also taking place during the gelation process.

Figure 4.3 Thermogram of quenched C₁₂ gel.

The gel to sol transition occurs over a broad temperature range, which is an indication of less co-operative phase transition (Figure 4.3). It can also be concluded from the thermogram that the packing of the molecules within the aggregates is much less ordered than within the crystals.

As the gel to sol transition occurs over a broad temperature range it is not possible to measure the exact heat of gelation. Therefore, breadth of the transitions i.e. ΔT and $\Delta T_{1/2}$

(ΔT is the width at full height and $\Delta T_{1/2}$ is the width at half height) were measured and presented in Table 4.1.

Table 4.1 Breadth of the endothermic transitions with respect to the alkyl side chain.

Sample I.D.	Quenched		Slow cooled	
	ΔT (°C)	$\Delta T_{1/2}$ (°C)	ΔT (°C)	$\Delta T_{1/2}$ (°C)
C ₆	13.7	5.2	17.0	8.2
C ₈	21.9	10.0	25.5	10.4
C ₁₂	21.4	8.7	28.6	10.0
C ₁₆	9.7	6.7	30.9	12.8
C ₁₈	9.0	5.1	27.6	5.9

There is not much difference observed in the breadth of the transitions i.e. ΔT and $\Delta T_{1/2}$ for the quenched C₈ and C₁₂ gels. However, beyond C₁₂, both the values decrease significantly. This shows that gelation is not favored in these cases of quenching. For the slow cooled gels both the values increase with the increasing alkyl side chain up to C₁₆. This demonstrates that gelation is favored with the increase in the alkyl side chain length when the gels are prepared by slowly cooling the bis-carbamates/ benzonitrile solution. The slow cooled C₁₈ showed a very different behavior compared to the other members of the series. The reason behind this will be discussed later.

It is interesting to note that the ΔT and $\Delta T_{1/2}$ values recorded for the slow cooled gels have always been found to be higher than their quenched counterparts. This shows that slowly cooling the solutions favor more gelation compared to the quenching them. (where as quenching of the solutions favor crystallization). The Figure 4.4 represents the endothermic thermograms recorded for the quenched and slow cooled C_8 gels.

Figure 4.4 Endothermic thermograms of slow cooled and quenched C_8 gels.

The reason behind quenching of the solution favoring less gelation (crystallization rather than gelation) could be that when the clear solutions are quenched in an ice-bath, the molecules don't get time to organize themselves in such a way as to form a strong network in order to hold the solvent. This leads to reduced gelation and favors normal

nucleation, which ultimately results in the destruction of gels and provides more opportunity for crystallization.

Compared to simple carbamates, all the counterpart members of bis-carbamates have shown high critical gelator concentration as well as high thermoreversible sol to gel transition temperatures. The same kind of trend has also been observed for the melting points of simple versus biscarbamates (Chapter 3). Moreover, simple carbamate members up to C₁₂ form gels and favor only gelation rather than gelation and crystallization like biscarbamates. The symmetry of the side chains on either side of the hydrogen bonding moiety in the case of the latter could be a contributing factor.

The analysis mentioned above demonstrates the effect of alkyl side chain length, single versus double hydrogen bonding motif as well as the process involved in making gels, on the thermal behavior of the gels. All the slow cooled gels have shown domination of gelation with the increase in the alkyl side chain length up to C₁₆. To investigate the reason behind the change in the thermal behavior of slow cooled C₁₈ gels with respect to the other members, one more dimension was added to the study viz. the effect of concentration particularly on this member (C₁₈) of the series.

4.3.4 Effect of Concentration

4.3.4.1 Critical Gelation Time

The slow cooled and quenched samples of different concentrations ranging from 0.02M to 0.06M in increments of 0.01M along with a concentration of 0.08M were studied. For the slow cooled gels it was found that the gelation time decreases with the increase in the concentration (Figure 4.5 a).

Figure 4.5 (a) Gelation time versus molar concentration of the C_{18} slow cooled gels.

4.3.4.2 Thermal Behavior of Different Concentrations of Gels

Here also two endothermic peaks appear, one each for the gel and the crystallized biscarbamates (Figure 4.5 b). This shows that gelation as well as crystallization was taking place at every concentration. For the quenched and slow cooled C_{18} gels, ΔT and

$\Delta T_{1/2}$ were recorded for each concentration and presented in Table 4.2. An increase in ΔT and $\Delta T_{1/2}$ is recorded for each sample i.e. quenched and slow cooled ranging from 0.02 to 0.05M concentration. A drastic decrease in these values has been noted for 0.06 and 0.08M concentration for both the gels. However, for each concentration of slow cooled gels these values have been found to be quite higher than the quenched counterparts. The same trend has been exhibited by the slow cooled gels with the increasing alkyl side chain length up to C_{16} . This again demonstrates that when the gels are prepared by slowly cooling the solution favor more gelation than quenching them. The maximum gelation i.e. the highest values of ΔT and $\Delta T_{1/2}$ have been shown by 0.04M C_{18} slow cooled gels. Therefore, gelation is favored more comparatively at low concentrations. At high concentration the decrease in ΔT and $\Delta T_{1/2}$ indicates a competition between gelation and crystallization.

Figure 4.5 (b) Endothermic thermogram of slow cooled C_{18} 0.04M gel.

Table 4.2 Breadth of the endothermic transitions with respect to the different concentrations of the C₁₈ gels.

Concentration	Quenched		Slow cooled	
	ΔT (°C)	$\Delta T_{1/2}$ (°C)	ΔT (°C)	$\Delta T_{1/2}$ (°C)
0.02M	15.7	6.5	29.9	7.6
0.03M	20.0	5.6	33.6	9.2
0.04M	23.3	6.3	37.6	9.3
0.05M	22.4	10.0	35.1	8.3
0.06M	12.7	6.1	28.9	8.0
0.08M	9.0	5.1	27.6	5.9

4.3.5 Morphology of the Xerogels (0.08M)

The morphology of the gels of biscarbamates is distinctly different from those of simple carbamates. The morphology in this case consists of shorter tapes, ribbons and hollow fibers depending on the length of the alkyl side chain and the method used for gelation (slow cooled versus quenched). The xerogels of quenched C₆ form irregular sheet or ribbon like structures. These sheets try to wrap, ultimately forming fibers (Figure 4.6 a). Wrapping of the sheets can result in the formation of hollow fibers. Only a small percentage of the sheets are successful in fiber formation. As a result, the population of sheets is more compared to the fibers. The fibers are not long and don't show

entanglement. This is the only member, which has shown stacking of the sheets. Their slow cooled counterparts form densely populated petal like structures (Figure 4.7 a). These gels were unable to form fibers. The C_8 quenched gels exhibit a combination of sheets and fibers. Like C_6 counterparts, wrapping has been found to be common here too. These gels also demonstrate the twisting of the fibers (Figure 4.6 b). The length of the C_8 fibers is more than that of C_6 . Similar to C_6 , the fibers of C_8 xerogels also don't show any entanglement. The fibers of slow cooled C_8 xerogels (Figure 4.7 b) are longer than their quenched counterparts. The quenched xerogels have a combination of wide and narrow fibers while the slow cooled xerogels form relatively uniform fibers. The quenched C_{12} fibers show entanglement or junctions up to a certain extent. The transparency of the fibers indicates that they are quite thin (Figure 4.6 c). A few fibers are bifurcated, and some very narrow fibers entangle themselves to form knot like structures. A web like morphology has also been seen in this particular kind of xerogel. The slow cooled C_{12} xerogels are denser than their quenched counterparts and don't show entanglement. Similar to quenched fibers they also have a combination of narrow and wide fibers, and are bifurcated (Figure 4.7c). The narrow fibers of quenched C_{16} xerogels (Figure 4.6 d) entangle with each other whereas the wide fibers don't show any kind of entanglement. The slow cooled fibers of C_{16} (Figure 4.7d) have been found to be densely populated compared to their C_{12} counterparts. The fibers show splitting at one of their ends. In all the cases the length of the fibers has been found to be more than their width. This indicates that the rate of growth is anisotropic, which is the result of a preferred orientation of the molecules within the sheets. The fibers of quenched C_{18} xerogels form a corolla like structure. This structure can result from the branching of the fibers and

(a)

(b)

(c)

(d)

(e)

Figure 4.6 The SEM images of quenched xerogels (a) C_6 (b) C_8 (c) C_{12} (d) C_{16} and (e) C_{18} .

Figure 4.7 The SEM images of slow cooled xerogels (a) C₆ (b) C₈ (c) C₁₂ (d) C₁₆ and (e) C₁₈

these branches further divide into daughter branches or there is a possibility that the fibers, which are already branched, overlap with each other and finally form a corolla-like structure (Figure 4.6 e). The density of the fibers is quite reduced in these xerogels and the fibers are short in length compared to C_{16} fibers. The slow cooled C_{18} xerogels result in a very different morphology than their quenched counterparts (Figure 4.7 e). They form very smooth fibers without any entanglements. Biscarbamates xerogels have shown very different morphology than simple carbamate xerogels. The latter xerogels form long, branched, entangled and rope like fibers³⁰.

4.3.6 Transverse Section of Slow cooled Xerogels

The SEM images reveal the stacking, and wrapping of the sheet in the case of quenched gels which creates a possibility that fibers obtained from the quenched as well as from the slow cooled gels can be hollow in nature. Therefore, the transverse section of the slow cooled xerogels C_{12} was studied under the SEM. Figure 4.8 a shows that there could be some hollow part in the center of the fiber. To confirm the hollow nature of the fibers the SEM image of the tip of the fiber was recorded and is shown in figure 4.8 b. Figure 4.8 c represents the same fiber tip but at a higher resolution. These figures confirm the hollow nature of the fibers of the slow cooled gels.

Figure 4.8 SEM images of the transverse section of C_{12} slow cooled xerogels.

4.3.7 Morphology of the Gels

To further confirm the hollow nature of the fibers, the morphology of quenched and slow cooled gels of different concentrations of C_{18} was studied using SEM under cryogenic conditions. The quenched gels of 0.03M concentration form a tape or ribbon like structure. These tapes arrange themselves in such a way as to form a cluster, creating a weed like morphology. Moreover, crystals were also found growing in between these fibers (Figure 4.9a). The slow cooled gels of the same concentrations show that the fibers are not yet formed and crystals as well as fibers are trying to form at the same time. Crystals are found to be embedded in the gel (Figure 4.10 a). The quenched gels of 0.04M show a similar morphology like the quenched 0.03M ones but the micrographs recorded at higher resolution show that the sheets are irregular in shape and are trying to

wrap to form fibers. Crystals have been found to be growing at the periphery of the bulk of sheets. However, some crystals have also been found to grow on top of the fibers (Figure 4.9 b). The slow cooled gels of 0.04M were able to form proper fibers. The wrapping of the sheets have been observed too. Moreover, some of the fibers are bifurcated (Figure 4.10 b). The transparency of the fibers shows that they are quite thin. A pronounced density of crystals has been found in the quenched samples of 0.05M gels (Figure 4.9 c). The slow cooled gels of 0.05M show sheet like structures (Figure 4.10 c) with a wrapping at the edges. This shows that these gels first form sheet like structures and then their wrapping takes place, ultimately leading to the formation of hollow fibers. The quenched 0.06M gels have shown the maximum population of crystals (Figure 4.9 d). The slowcooled 0.06M gels have shown the combination of wide and narrow fibers (Figure 4.10 d).

Figure 4.9 The SEM images (cryo condition) of quenched gels of different C_{18} concentrations (a) 0.03M (b) 0.04M (c) 0.05M and (d) 0.06M.

100 μm

(a)

Transparent

Bifurcation

100 μm

10 μm

(b)

10 μm

10 μm

(c)

(d)

Figure 4.10 The SEM images (cryo condition) of slow cooled gels of different C_{18} concentrations (a) 0.03M (b) 0.04M (c) 0.05M and (d) 0.06M.

4.3.8 Aging of the Gels

To further prove the validity of the argument, aging of the C_8 and C_{18} slow cooled gels was studied. In both the cases freshly prepared gels showed a sheet-like structure (Figure 11a and 12a respectively) with wrapping at the edges. The micrographs recorded for both the samples a week later under SEM (Figure 11b and 12 b) showed that the sheets are almost completely wrapped leaving behind very thin slits. When the micrographs of the same samples were recorded the week after, these gel platelets or sheets were fully transformed into fibers (Figure 11c and 12c).

Figure 4.11 SEM images (cryo condition) of C_8 gel (a) 1st (b) 7th and (c) 14th day.

Figure 4.12 SEM images (cryo condition) of C₁₈ gel (a) 1st (b) 7th and (c) 14th day.

4.3.9 Effect of Shear Rate

In order to determine the growth direction of the hydrogen bonded sheet, in the previous study on simple carbamates the gel fibers were gently stroked with fingers to impart some orientation. In the present case, attempt has been made to induce such orientation in situ, by applying rotational shear in situ. A shear was applied at different rpm speed (70, 70 with pause, 80, 100, 110) using the magnetic stirrer bar (size:5x2 mm) during the preparation of 0.08M slow cooled C_{18} gels. The morphology of gels and xerogels was studied for all the samples obtained at the various speeds. The xerogels were obtained from their corresponding gels after the removal of the solvent (benzonitrile). The comparison of Figures 4.13 a and b shows that the fibers are densely populated in the case of xerogels obtained at 70 rpm rather than 70 rpm with pause. However, the average thickness of the fibers has been found to be more in the latter case compared to the former one. The reason could be that when the gels were prepared by pausing the stirring action, the molecules got the required amount of time to form more layers of the molecular chains, leading to the formation of wider fibers. The fibers of the xerogels prepared at 80 and 100 rpm (Figure 4.13 c and d respectively) were longer than obtained at 70 and 110 rpm (4.13 e). The density of the fibers was less when obtained at 80 rpm as compared to 100 rpm. The well-oriented fibers were only seen in the case of xerogels obtained at 100 and 110 rpm. However, the fibers at 110 rpm (Figure 4.13 e) were found to be the shortest among this series. The reason could be that the fibers might not have been able to handle that much stress. All the gels obtained from different shear levels have shown the existence of hollow fibers. Figures 4.13 f and g represent the SEM images recorded for the gels prepared at 70 and 110 rpm speed under cryo conditions

respectively. Both the images further confirm the hollow nature of the fibers similar to the aging case discussed before and the images obtained from the transverse section of the fibers as mentioned earlier. Therefore, different kinds of fibers like short, long, dense or less dense can be tailored according to the requirements by applying different shear levels. The shear effect has not been found to affect the process of fiber formation i.e. wrapping of the sheets or platelets leading to the formation of fibers.

4.3.10 IR Spectra

All the slow cooled and quenched gels showed hydrogen bonded C=O and N-H stretching vibrations. The C₆ quenched and slow cooled gels showed non-hydrogen bonded C=O and N-H stretching vibrations also. The absorbance position of H-bonded N-H stretching vibration was recorded at $\approx 3321\text{ cm}^{-1}$ for all the gels except the quenched C₁₈, where it was recorded at 3317 cm^{-1} . Similarly, the absorbance position of H-bonded C=O stretching was observed at $\approx 1683\text{ cm}^{-1}$.

The absorbance positions for the asymmetric CH₂ vibrations were recorded for both the quenched and slow cooled samples. In both the cases a decrease in absorbance position is recorded with an increase in the alkyl chain length. The quenched gels ranging from C₆ to C₁₂ showed the same values of absorbance positions as recorded for their slow cooled counterparts. The C₁₆ and C₁₈ slow cooled gels have shown higher absorbance value compared to the quenched gels of the same alkyl side chain length (Figure 4.14). In the previous chapter (Chapter 3) it was mentioned that the absorbance of asymmetric CH₂ at

Figure 4.13 SEM images of the 0.08M slow cooled C_{18} xerogels after applying different levels of shear (a) 70 (b) 70 with pause (c) 80 (d) 100 (e) 100 rpm; gels (cryo condition) (f) 70 and (g) 110rpm.

higher wave number indicates stronger high hydrogen bonding interactions. Therefore, it can be concluded that with the increase in the alkyl side chain length, the relative contribution of the hydrogen bonding interactions decrease as compared to the van der Waals interactions. The increase in van der Waals interactions for the quenched C₁₆ and C₁₈ has been found to be more pronounced than their slow cooled counterparts.

Figure 4.14 Wavenumber (cm⁻¹) of asymmetric CH₂ stretching vibrations for various alkyl side chain lengths.

The same kind of trend has been seen in the ΔT and $\Delta T_{1/2}$ values with respect to the quenched and slow cooled C₁₆ and C₁₈ gels i.e. more gelation was observed for the slow cooled C₁₆ and C₁₈ compared to the quenched members. Therefore, it can be concluded that in the slow cooled gels due to the comparatively lower van der Waals interactions

and molecules getting more time to organize themselves to form a network to hold the solvent resulted in more gelation than crystallization.

4.3.11 X-ray Diffraction

The X-ray patterns were recorded for the oriented xerogels obtained from C₁₈ 0.08M slow cooled gels prepared by applying the shear at 100 rpm. The diffractions were recorded using the flat film camera. The xerogels were mounted on the collimator and optical micrographs were recorded to know which fibrillar part is going to be exposed under the X-ray beam. Figure 4.15a shows the optical micrograph of exposed fibrillar part of slow cooled C₁₈ xerogel and Figure 4.15 b is the X-ray pattern obtained from it. The reflections 3.8 and 4.6Å have been found to be common here also as observed in the case of slow cooled samples prepared from the melt. The meridian reflection at 4.6Å marks the distance between two hydrogen bonded biscarbamate molecules. The equatorial reflection at 3.8Å accounts for the distance between the two layers of the molecules. In the previous sections the hollow nature of the fibers has been proved. A model has been made which shows the arrangement and wrapping of the molecules forming a sheet and ultimately forming a hollow fiber (Figure 4.15 c).

Figure 4.15. (a) Optical micrograph of C_{12} xerogels exposed under X-ray (b) X-ray diffractogram (c) schematic of orientation and wrapping of the molecules leading to the formation of hollow fiber.

The previous studies done on the simple carbamates by our group³⁰ and Terech et.al.,³² also found that the molecular packing in the compounds does not change by gelating the compounds, i.e. they stay the same. Therefore, on the basis of our previous and present studies we can conclude that the reflections at 4.6 and 3.8 Å on the meridian and equatorial respectively show that the fibers are growing in the direction of the hydrogen bonding plane 4.6 Å and the distance between the layers of two hydrogen bonding plane is 3.8 Å.

4.4 Conclusions

The work presented in this chapter has set a very good example of effect of single versus double hydrogen bonding motifs on the morphology of the self-assembling molecules. All the biscarbamates members under present study are able to form gels. Some similarities have been observed between the biscarbamates and simple carbamates gels. Similar to simple carbamates, biscarbamates showed a decrease in the critical gelator concentration and gelation time and an increase in the gelation temperature with the increase in the length of the alkyl side chain.

In spite of similarities, biscarbamates behave very differently compared to the simple carbamates. In the case of simple carbamates, only few members (C₄ to C₁₂) were able to form gel. Their C₁₆ and C₁₈ members favor crystallization only. This could be due to their high percent crystallinity and heat of fusion. However, all the members of biscarbamates used for the present studies form gel. The DSC study has shown that the heat of fusion of biscarbamates increases sharply from C₄ to C₈ and later on increases gradually with the

increase in the length of the alkyl side chain length and is mentioned in the previous chapter (Chapter 3).

The DSC results of the biscarbamates have also shown that in both the cases (slow cooled and quenched) gelation as well as crystallization was taking place at the same time. The thermoreversible gel to sol transitions occurred in a wide range therefore, the breadth of the transitions i.e. ΔT and $\Delta T_{1/2}$ were measured. Higher value of ΔT and $\Delta T_{1/2}$ indicate more gelation. These values have been found to increase with the increase in the alkyl side chain length up to C_{16} for the slow cooled and until C_{12} for the quenched gels. However, each slow cooled gel has shown a higher value for ΔT and $\Delta T_{1/2}$ compared to their quenched counterparts. This shows that slowly cooling the solution biscarbamates/benzonitrile favors more gelation rather than quenching. ΔT and $\Delta T_{1/2}$ values recorded for the slow cooled C_{18} have been found to be less compared to the C_{16} slow cooled gel. Therefore different concentrations of the C_{18} member were studied ranging from 0.02M to 0.06M with an increment of 0.01M along with the 0.08M. Both the quenched and slow cooled gels have shown that the ΔT and $\Delta T_{1/2}$ values increase from 0.02M to 0.05M and after that they decrease. This shows that up to a certain concentration gelation is favored and later on the competition between gelation and crystallization becomes tough and results in the domination of crystallization over gelation.

The IR results of the slow cooled and the quenched gels of 0.08M have shown that with the increase in the alkyl side chain length the absorbance position of the asymmetric CH_2 vibration decreases. This decrease has been observed to be more pronounced for the

quenched C₁₆, C₁₈ and slow cooled C₁₈ compared to the rest of the gels. The decrease in the position of the absorbance of the CH₂ vibrations dictates the increase in the van der Waals interactions.

On comparing the DSC and IR results obtained for the quenched C₁₆, C₁₈ and slow cooled C₁₈ gel a direct correlation can be drawn. ΔT and $\Delta T_{1/2}$ values have been found to be lowest for C₁₆ and C₁₈ in the series of quenched gels and the same members have shown a more prominent decrease in the absorbance position of CH₂ asymmetric vibrations compared to the rest of the quenched members. This shows the domination of van der Waals interactions resulting in less gelation and more crystallization. The same correlation can be drawn for the slow cooled C₁₈ (0.08M) gels which has shown a decrease in ΔT and $\Delta T_{1/2}$ values compared to C₁₆ slow cooled gels. This can again be rationalized due to the pronounced decrease observed in the absorbance position of the CH₂ asymmetric vibrations for C₁₈ compared to C₁₆ slow cooled gels.

The morphology of the biscarbamates xerogels has been found to be totally different from the simple carbamate xerogels. The SEM micrographs recorded for the quenched and slow cooled xerogels of biscarbamates showed that all the members form fibers except for the C₆ slow cooled ones. The fibers formed in the case of biscarbamates have been found to be shorter than their simple carbamates counterparts. Also fibers of biscarbamates do not entangle with each other up to such a extent as seen in the fibers of the simple carbamates.

Some quenched gels have shown wrapping and twisting of the fibers, which gave an impression that the fibers of biscarbamates can be hollow in nature. Therefore, the transverse section of the slow cooled C_{12} fiber was studied under the SEM, showed that the fiber is hollow. To further prove the validity of the argument, quenched and slow cooled gels of different concentrations of the C_{18} were studied. The SEM micrographs recorded under the cryo condition have shown wrapping of the sheets. Especially the sheets formed by the 0.05M concentration (slow cooled) clearly show wrapping at the edges. In addition, aging of the C_8 and C_{18} members (0.05M) was studied. The SEM images that were recorded on the same day when the gels were prepared showed a sheet like morphology with wrapping at the edges. A week later these sheets were found to be wrapped almost completely leaving behind a slit and the following week all these partially wrapped sheets were observed to be transformed into the fibers.

The shear effect has also been found to affect the morphology of the gels. The SEM micrographs of the gels obtained at different rpm speed have again proved the hollow nature of the gels. Well-oriented fibers were formed in the gels made at 100 and 110 rpm speeds. The X-ray diffractograms recorded for slow cooled xerogels have also shown the equatorial and meridian reflections at $4.6\text{\AA}$ and $3.8\text{\AA}$ respectively. This pattern is identical to the reflections observed when the samples were slowly cooled from the melt (Chapter 3) indicates that molecular packing is still the same and not disturbed. Hence we conclude that the growth of the fibers is in the direction of the hydrogen-bonding plane and the distance between the hydrogen bonding sheets is $3.8\text{\AA}$.

4.5 References

1. Garlaschelli, G.; Ramaccini, F.; Della Sala, S. *Nature* **1991**, 353, 507.
2. (a) Graham, T. *Trans. R. Soc.* **1861**, 151, 183.
(b) Graham, T. *J. Chem. Soc.* **1864**, 17, 318.
3. (a) Corriu, R.J.P.; Leclercq, D. *Angew. Chem., Int. Ed.* **1996**, 35, 1420.
(b) Reetz, M.T. *Adv. Mater.* **1997**, 9, 943.
4. (a) Lin, Y.-C.; Weiss, R.G. *Macromolecules* **1987**, 20, 414.
(b) Murata, K.; Aoki, M.; Nishi, T.; Ikeda, A.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1991**, 1715.
(c) Mukkamala, R.; Weiss, R. *Langmuir* **1996**, 12, 1474.
(d) Geiger, C.; Stabescu, M.; Chen, L.; Whitten, D.G. *Langmuir* **1999**, 15, 2241.
5. Pilpel, N. *Chem. Rev.* **1963**, 63, 221.
6. Uzu, Y.J. *Jpn. Oil Chem. Soc.* **1975**, 24, 261.
7. (a) Yamamoto, S. *J. Soc. Chem. Ind. Jpn.* **1943**, 46, 279-281.
(b) Taravel, F.R.; Pfannemueller, B. *Makromol. Chem.* **1990**, 191, 3097.
(c) Yamasaki, S.; Tsutsumi, H. *Bull. Chem. Soc. Jpn.* **1994**, 67, 2053.
(d) Hafkamp, R.J.H.; Feiters, M.C.; Nolte, R.J.M. *J. Org. Chem.* **1999**, 64, 412.
(e) Beginn, U.; Keinath, S.; Moller, M. *Macromol. Chem. Phys.* **1998**, 199, 2379.
(f) Yoza, K.; Amanokura, N.; Ono, Y.; Akao, T.; Shinmori, H.; Shinkai, S.; Reinhoudt, D.N. *Chem.-Eur. J.* **1999**, 5, 2722.
8. (a) de Vries, E.J.; Kellogg, R.M. *J. Chem. Soc., Chem. Commun.* **1993**, 238

- (b) Aggeli, A.; Bell, M. Boden, N.; Keen, J.N.; Knowles, P.F.; McLeish, T.C.B.; Pitkeathly, M.; Radford, M. *Nature* **1997**, *386*, 259.
9. Campbell, J.; Kuzma, M.; Labes, M. *Mol. Cryst. Liq. Cryst.* **1983**, *95*, 45.
10. Hanabusa, K.; Tange, J.; Taguchi, Y.; Koyama, T.; Shirai, H. *J. Chem. Soc., Chem. Commun.* **1993**, 390.
11. (a) Terech, P.; Gebel, P.; Ramasseul, R. *Langmuir* **1996**, *12*, 4321.
- (b) Engelkamp, H.; Middelbeek, S.; Nolte, R.J.M. *Science* **1999**, *284*, 785.
12. Abdallah, D.J.; Weiss, R.G. *Langmuir* **2000**, *16*, 352.
13. (a) Hanabusa, K.; Shimura, K.; Hirose, K.; Yamada, M.; Shirai, H.; *Chem. Lett.* **1996**, 885.
- (b) Shi, H.; Huang, Z.; Kilic, S.; Xu, J.; Enick, R.M.; Beckman, E.J.; Carr, A.J.; Melendez, R.E.; Hamilton, A.D. *Science* **1999**, *286*, 1540.
14. (a) van Esch, J.; De Feyter, S.; Kellogg, R.M.; De Schryver, F.; Feringa, B.L. *Chem.-Eur. J.* **1997**, *3*, 1238.
- (b) de Loos, M.; van Esch, J.; Stokroos, I.; Kellogg, R.M.; Feringa, B.L. *J. Am. Chem. Soc.* **1997**, *119*, 12675.
- (c) van Esch, J.; Schoonbeek, F.; de Loos, M.; Kooijman, H. Spek, A.L.; Kellogg, R.M.; Feringa, B.L. *Chem.-Eur. J.* **1999**, *5*, 937.
15. Murata, K.; Aoki, M.; Susuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664.
16. Terech, P.; Weiss, R.G. *Chem. Rev.* **1997**, *97*, 3133.
17. Sobna, J-E. S.; Fages, F. *Chem Commun.* **1997**, 327.

18. Hanabusa, K.; Maesaka, Y.; Kimura, M.; Shirai, H. *Tetrahedron Lett.* **1999**, *40*, 2385.
19. Kimura, T.; Yamashita, T.; Koumoto, K.; Shinkai, S. *Tetrahedron Lett.* **1999**, *40*, 6631.
20. Bhattacharya, S.; Acharya, S.N.G. *Chem. Mater.* **1999**, *11*, 3121.
21. (a) Ajaygosh, A.; George, S.J.; Praveen, V.K. *Angew. Chem., Int. Ed.* **2003**, *42*, 332.
- (b) Urabe, H.; Jung, J.H.; Ono, Y.; Shinkai, S.; Soai, K. *Tetrahedron Lett.* **2003**, *44*, 721.
- (c) Tiller, J.C. *Angew. Chem., Int. Ed.* **2003**, *42*, 3072.
- (d) Friggeri, A.; Feringa, B.; van Esch, J. *J. Controlled Release* **2004**, *97*, 241.
- (e) Roubeau, O.; Colin, A.; Schmitt, V.; Clerac, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 3283.
- (f) Yang, Z.; Gu, H.; Fu, D.; Gao, P.; Lam, J.K.; Xu, B. *Adv. Mater.* **2004**, *16*, 1440.
- (g) Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229.
- (h) Yao, S.; Begnin, U.; Gress, T.; Lysetska, M.; Wurthner, F. *J. Am. Chem. Soc.* **2004**, *126*, 8336.
- (i) Kiyonaga, S.; Sada, K.; Yoshimura, I.; Shinkai, S.; Kato, N.; Hamachi, I. *Nat. Mater.* **2004**, *3*, 58.
22. Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664.

23. Henisch, H.K. *Crystal growth in Gels* Pennsylvania State University Press: University Park, PA, 1970.
24. Srivastava, S.P.; Saxena, A.K.; Tendon, R.S.; Shekhar, V. *Fuel* **1997**, 625.
25. Shi, C.; Huang, Z.; Kilic, S.; Xu, J.; Enick, R.M.; Beckman, E.J.; Carr, A.J.; Melendz, R.E.; Hamilton, A.D. *Science* **1999**, 286, 1540.
26. van Esch, J.; Schoonbeek, F.; de Loos, M.; Veen, E.M.; Kellogg, R.M.; Feringa, B.L. *Nato ASI Ser. C* **1999**, 527, 233.
27. (a) Hanabusa, K.; Yamada, M.; Kimura, M.; Shirai, H. *Angew. Chem., Int. Ed.* **1996**, 35, 1949.
- (b) Lin, Y.; Kachar, B.; Weis, R.G. *J. Am. Chem. Soc.* **1989**, 111, 5542.
- (c) Yoza, K.; Amanokura, N.; Ono, Y.; Aoka, T.; Shinmori, H.; Takeuchi, M.; Shinaki, S.; Reinhoudt, D.N. *Chem. Eur. J.* **1999**, 5, 2722.
- (d) van Esch, J.; Schoonbeek, F.; de Loos, M.; Veen, E.M.; Kellogg, R.M.; Feringa, B.L. *Chem. Eur. J.* **1999**, 5, 937.
28. Jazdzyn, J.; Stockhausen, M.; Zywicki, B. *J. Phys. Chem.* **1987**, 91, 754.
29. van Esch, J.; Kellogg, R.M.; Feringa, B.L. *Tetrahedron Lett.* **1997**, 38, 281.
30. Moniruzzaman, M.; Sundararajan, P.R. *Langmuir*, **2005**, 21, 3802.
31. Liangde Lu, T.; Cocker, M.; Bachman, R.E. Weis, R.G. *Langmuir*, **2000**, 16, 20.
32. Terech, P.; Rodriguez, V.; Barnes, J.D.; McKenna, G.B. *Langmuir*, **1994**, 10, 3406.

Chapter 5

Conclusions and Recommendations for Future Work

5.1 Conclusions

In the introduction section (Chapter 1) the affect of different non-covalent interactions i.e. hydrogen bonding, van der Waals interactions, π -stacking etc. on morphology of the self-assembling molecules has been discussed. In certain cases more than one of theses factors have been found to be responsible for the self-assembly of the molecules. Instead of synthesizing new molecules, one can tailor the existing molecules as per their requirements by just changing the morphology of the molecules. No doubt, self-assembly of the molecules due to certain interactions, has opened new gateways for the dawn of new and sophisticated materials.

The symmetry of the molecules as well as the number of hydrogen bonding motifs involved in the self-assembly of the molecules significantly affect the morphology of the molecules. For the simple carbamates, there was not much change observed in the size of the spherulites except for C₁₈, which has shown the largest spherulite size compared to the other members of the series. However, in the case of biscarbamates C₈ has shown the largest sized spherulites. This behavior has been rationalized on the basis of nucleation rate. The nucleation rate has been found to be controlled by a combination of hydrogen bonds and van der Waals energy involved in the packing of the two molecules. The van der Waals attractions between the segments increases with an increase in the alkyl side chain length. This has been proven by the shifts recorded for the CH₂ frequency towards lower wavelength with respect to the increasing alkyl side chain length.

The gelation properties of the biscarbamates have also been found to be different from the simple carbamates. In the case of simple carbamates only short alkyl side chain lengths (C₇-C₁₂) were able to gelate the solvent (benzonitrile) whereas long alkyl side chain length (C₁₆ and C₁₈) favored only crystallization. All the members of biscarbamates were able to form gel. However, all these members have shown gelation as well as crystallization at the same time. The interesting thing to notice here is that the slow cooled samples have favored more gelation rather than crystallization and this behavior has become pronounced with the increasing alkyl side chain length up to C₁₆. In the case of quenched samples crystallization has been found to be dominated over gelation and it increases with the increase in the length of the alkyl side chain length up to C₁₆. In the case of quenched and slow cooled C₁₈, the heat of gelation has been found to be the same as heat of crystallization. This is due to the effect of higher molar concentration. The most fascinating property of the xerogels is the hollow nature of the fibers. The hollow nature of the fibers has been proved by the SEM images of the transverse section of the fiber, gels and aging of the gels under cryogenic conditions, and the images recorded to study the effect of shear effect on the fibers. These fibers can be well –oriented at a particular shear rate applied during the gel formation. The hollow nature of the fibers has not been shown by the gels or xerogels of the simple carbamates. The fibers of the simple carbamates were found to be comparatively longer than their quenched counterparts.

5.2 Recommendations for Future Work

The present study has shown the profound effect of length of the alkyl side chain, symmetry of the molecules and double hydrogen-bonding motif versus single hydrogen-bonding motif on the morphology of the self-assembling biscarbamates. A similar study can also be done on related self-assembling molecules such as inverse biscarbamates.

The present work done on aliphatic biscarbamates has shown the effect of combination of hydrogen bond and van der Waals interactions on the morphology of the self-assembling molecules. It will be good to study the different alkyl side chain lengths of aromatic biscarbamates, which will introduce one more interaction i.e. π -stacking in the existing interactions controlling the morphology of the compounds.

Appendix A

IR Spectra of the Biscarbamates

C₄

C₆

C₈

C₁₂

C₁₈

Appendix B

^1H NMR Spectra of the Biscarbamates