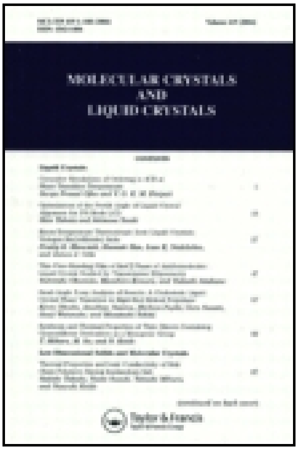

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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# Liquid Crystalline Polyethers

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# LIQUID CRYSTALLINE POLYETHERS

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Abstract The first part of this paper will review recent work from our laboratory on structural principles and their use in the synthesis of thermotropic-lyotropic main chain liquid crystalline (LC) polyethers. Two synthetic procedures, i.e., phase transfer catalyzed polyetherification and cationic ring opening polymerization of bridged bicyclic ethers will be described, and examples will be provided for the synthesis of polyethers containing flexible spacers, and of quasi-rigid polyethers. A detailed discussion will be made on the influence of microstructural parameters such as constitutional isomerism, sequence distribution, composition, and of molecular weight, on the phase transitions of LC copolyethers. The second part of this paper will briefly discuss some of the first examples of micro-phase separated biphasic side chain LC polymers, i.e., polymers exhibiting two glass transition temperatures, one due to the independent motion of the main chain, the other due to the cooperative but independent motion of the side groups. Their behavior suggests that the miscibility between side groups and main chain has to be considered by the space concept in order to achieve highly decoupled side chain LC polymers.

## INTRODUCTION

The traditional class of thermotropic and/or lyotropic main chain liquid crystalline polymers (LCP) are polyesters and polyamides, with very few examples of polycarbonates and polyurethanes. Recent reviews describing this field are available[1,2]. In spite of their commercial success, most of these polymers exhibited limited solubility in exotic solvents, and present high thermal transition temperatures which many times are well above the range of temperatures of the available laboratory instrumentation. Consequently, the synthesis of the above polymers with well defined molecular weights, molecular weight distribution and chain ends does not represent a trivial synthetic experiment. Last but not least, it is well established that polyesters, polyamides, polycarbonates and polyurethanes undergo reactions in solid state. For the case of LC copolyesters Lenz <u>et al</u>. have elegantly demonstrated that "crystallization induced reactions" are drastically changing the sequence distribution depending whether the polymer was thermally treated within the crystalline, anisotropic, or isotropic phase[3,4]. Since all the commercially and academically available LC polyesters are copolymers, it is difficult to assume that thermodynamic information obtained under equilibrium conditions, therefore requiring long annealing times at a certain temperature, are reported on correct copolymer sequence distributions and molecular weight. Therefore, it seems to be quite important to have available a class of LCP free of the above mentioned drawbacks, in order to be able to perform "textbook" type experiments.

Polyethers are known to be much more soluble than the corresponding polyesters or polyamides and undergo thermal transitions at lower temperatures, are hydrolytically stable, do not undergo thermal induced reactions, can be prepared with well defined chain ends and therefore seem to represent an ideal LCP system useful for a large variety of fundamental investigations. The first thermotropic main chain LCP was reported in 1984 from our laboratory[5,6] and soon thereafter Keller[7] followed by several other research groups became interested in this class of LCP.

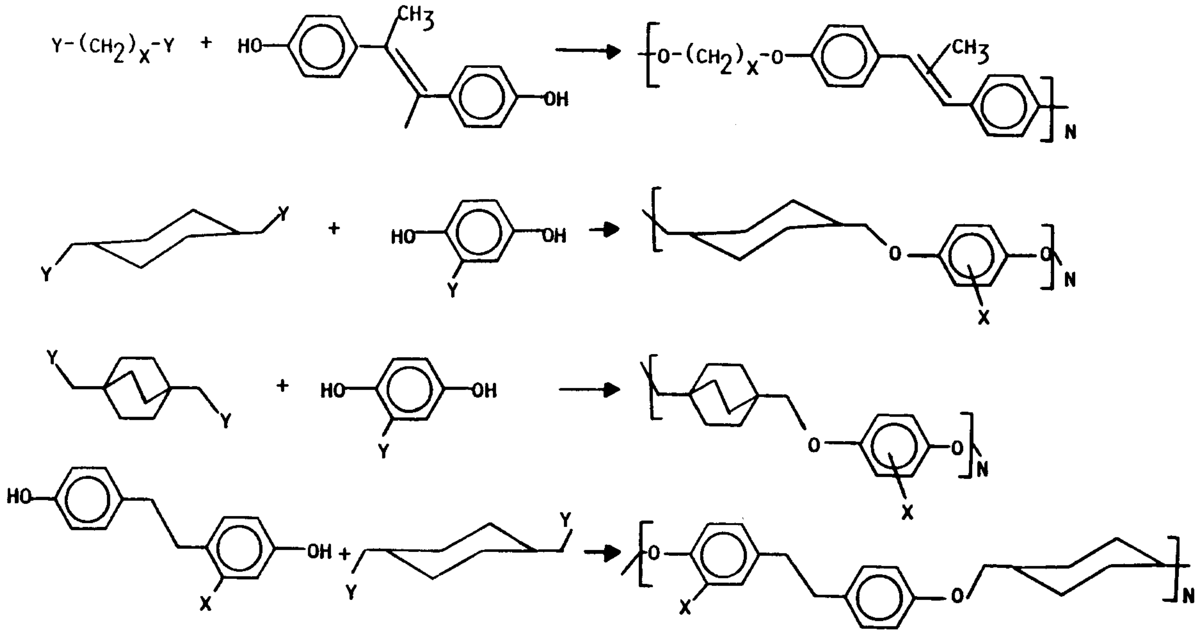
The first goal of this paper is to review some of our recent experiments performed in order to elucidate the structural principles requested in the synthesis of thermotropic-lyotropic main chain liquid crystalline polyethers with and without flexible spacers, as well as to discuss some of the first microstructure-molecular weight phase transition rules resulted from these studies.

The second goal of this paper is to briefly review some of our work on the elucidation of the spacer concept advanced by the classic papers of Ringsdorf, Finkelmann and Wendorff[8,9], as a tool to decouple the motion of the side groups from that of the main chain in side chain liquid crystalline polymers[10-12].

## LC POLYETHERS: SYNTHESIS AND STRUCTURAL PRINCIPLES

There are two conventional synthetic procedures which can be presently employed for the synthesis of polyethers: nucleophilic displacement reactions of reactive biselectrophilic compounds by bisnucleophilic derivatives, and cationic ring-opening polymerization of cyclic ethers.

The first reaction proceeds through a $S_N2$ mechanism and the most important requirement of this polymerization is a solvent which can dissolve both the deprotonated (usually in the form of a sodium or potassium salt) bisnucleophile, and the resulting polymer. Unfortunately, the only solvents providing this solubility characteristics are dipolar aprotic solvents which are not good solvents for any of the structures suspected as being potential candidates for polymers exhibiting liquid crystalline properties (Scheme 1). Therefore, at the present time, the only available method for their synthesis consists in the use of phase



Scheme 1: Synthesis of LC Polyethers by phase transfer catalyzed polyetherification.

transfer catalyzed (PTC) polyetherification. The principles of PTC polyetherification were recently reviewed[13] and the limited time and space will make us summarize only some of its particularities. For a two phase system (aqueous base , and an aqueous base non-miscible solvent which dissolves the resulting polymer) it is essential to use the proper reaction conditions and type of phase transfer catalyst which give the required extraction constant of the phase transfer catalyst paired bisnucleophile, so that the bisnucleophile gets transferred into the organic phase. These requirements are entropically controlled, and therefore only the structure of the ion-pair and the nature of the solvent used are dictating the conditional extraction constant. Therefore, for a certain bisnucleophilic monomer, there are only two parameters which can be controlled: the nature of the solvent and of the phase transfer catalyst. The overall rate constant of polyetherification depends on the concentration of reactants and can be adjusted as a function of the solubility of the resulting polymer. It is important to mention that all the polyethers outlined in Scheme 1 are both lyotropic and thermotropic. Since they are lyotropic we can employ very high initial concentrations of reactants (i.e., resulting in up to 50 wt % final polymer concentrations) and still take advantage of a relatively low viscosity of the reaction mixture. In addition, since in the lyotropic phase the macromolecules have a chain extended conformation, no cyclic polymers or oligomers result from this reaction. Therefore, this quasi-interfacial (from the stoichiometric point of view) solution polymerization leads under proper reation conditions to very high molecular weight polymers containing systematically only dielectrophilic chain ends[14,15]. The degree of polymerization is usually determined by the excess of dielectrophile[16] and not nucleophile as is the case in conventional polyetherifications[17].

The structural principles used in the synthesis of LC polyethers containing flexible spacers are similar to those used in the synthesis of LC polyesters, i.e. a pro-mesogenic bisphenol as for example 4,4'-dihydroxy-α-methylstilbene is copolymerized with dielectrophilic flexible spacers which can be either of parafinic[5-7] or oligooxyethylenic nature[18].

The synthesis of LC polyethers without flexible spacers, i.e., exhibiting a quasi-rigid character, is based on the use of structural units which exhibit

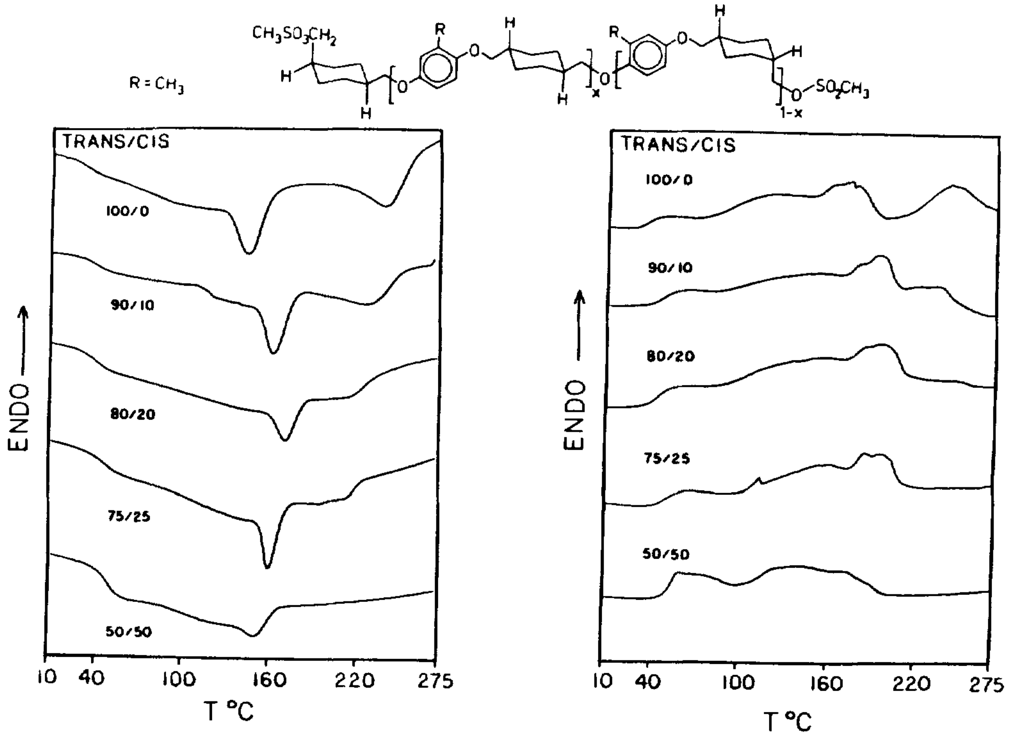
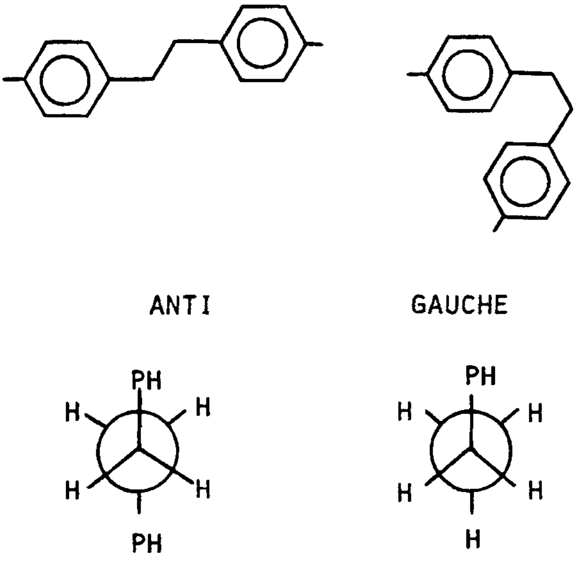


Figure 1: Some representative heating (right) and cooling (left) DSC thermograms of the polyethers and copolyethers based on methylhydroquinone and trans- and cis-1,4-bis(methane-sulfonylmethyl) cyclohexane.

conformational isomerism, i.e., diphenyl ethane, methylene ether or benzyl ether (Schemes 1, 2). Scheme 2 outlines this concept. Although there is free rotation around the C-O or C-C bonds, the two most stable conformational isomers are anti and gauche. The anti conformer has an extended conformation which in principle should behave as an aromatic rigid rod-like ester linkage. Therefore, any of the LC polyethers



Scheme 2: Conformational isomerism of diphenylethane, benzyl ether and methylene ether units.

synthesized based on this principle (Scheme 1) are in fact copolyethers which have a dynamic composition, and which can be assimilated with copolyesters based, for example, on terephthalic acid and a mixture of hydroquinone and resorcinol or catechol. Since the composition or ratio between these two isomers is in a dynamic equilibrium, these polyethers present much lower transition temperatures than the corresponding polyesters. For example, Figure 1 presents some differential scanning calorimetric results on LC polyethers obtained from methylhydroquinone and trans or a mixture of trans and cis cyclohexane-1,4-dimethanol based dielectrophiles[19]. As the corresponding polyesters based on trans 1,4-cyclohexane dicarboxylic acid and methylhydroquinone[20], all these polyethers exhibit two crystalline transitions followed by a nematic mesophase. Alternatively, as Figure 2 shows, methyl substituted 4,4'-dihydroxydiphenylethane based polyethers and copolyethers represent the first examples of LC polymers containing flexible spacers and no mesogenic rigid units. The conformational isomerism of the diphenylethane units induces in all cases at least a smectic and a nematic mesophase. With the exception of the copolyether containing nine and eleven methylene units in the spacer, all the other polyethers do not crystallize. Nevertheless, at this time at least for the case of the copolyethers containing five and seven and five and nine methylene units in the spacer, not only the composition of the copolymer is dynamic, but also its mesophase. The copolymer 5/7 exhibits a

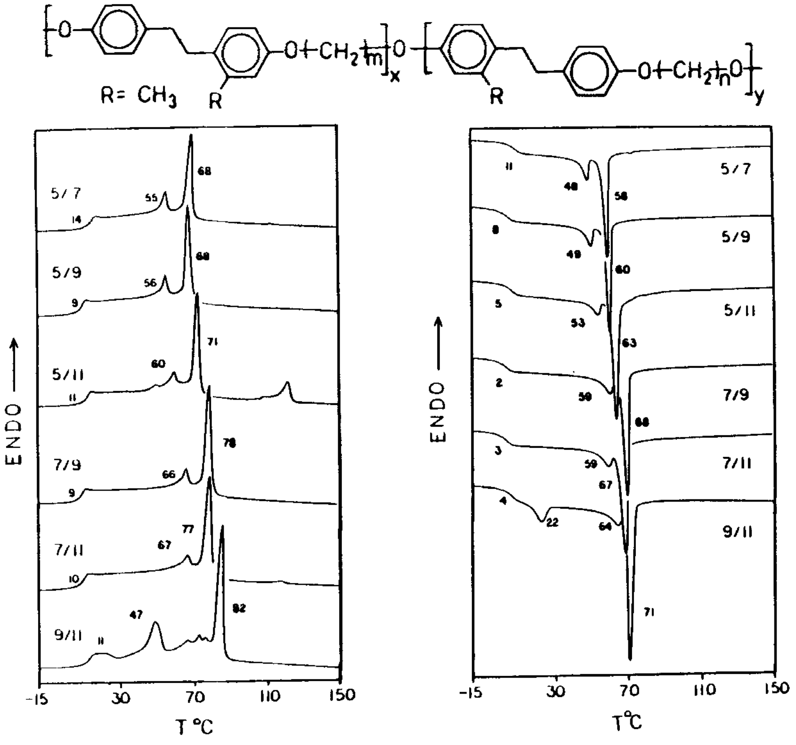
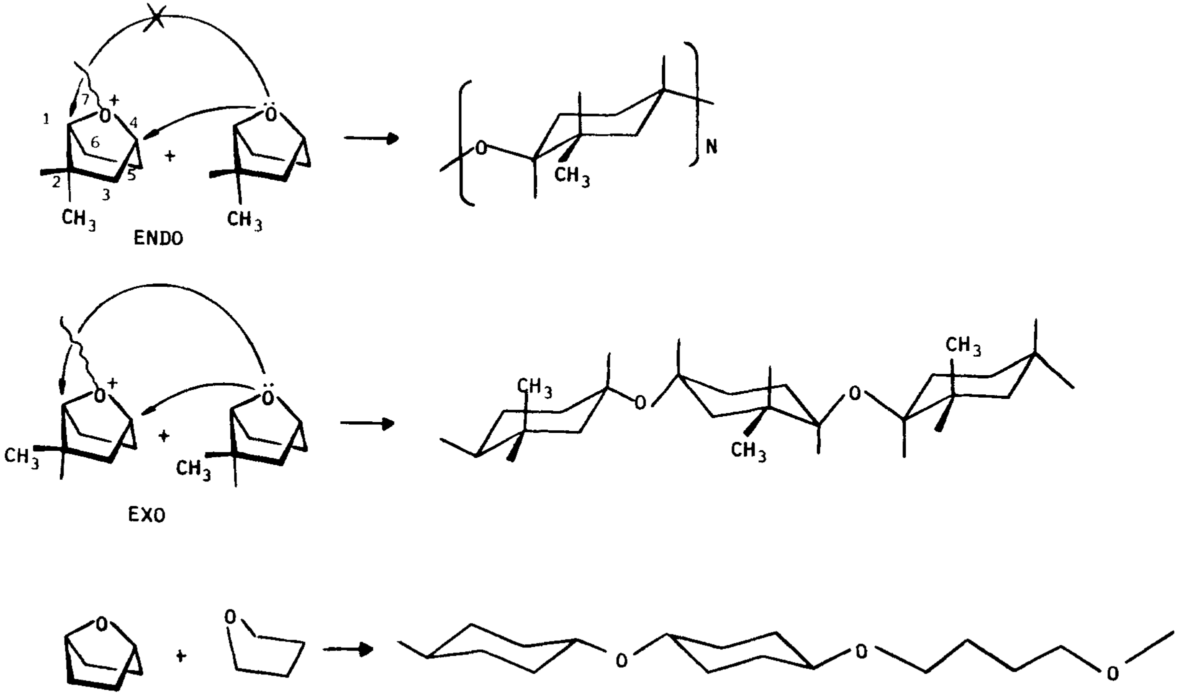


Figure 2: Representative heating (left) and cooling (right) DSC thermograms of the copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane and a 1/1 mole ratio between different spacers.

nematic mesophase in between 55 and 68° C on the heating scan (20° C/min). Annealing the polymer at 64.1° C, the mesophase becomes smectic both according to optical polarization microscopy, and to isotropization enthalpy. These experiments are opening a series of fundamental questions related to conformational isomerism within isotropic versus anisotropic phases, and before more information is obtained on this topic, it might be difficult to completely understand the relationship between dynamic composition and dynamic mesophase. Additional details on this subject are going to be published soon[19]. Nevertheless, at the present time, we can safely state that the synthesis of thermotropic LC polyethers based on calamitic-like mesogens, does not necessarily require rigid rod-like mesogenic units. They can also be obtained from flexible molecules exhibiting conformational isomerism and which can give rise to extended conformations.

The synthesis of thermotropic LC polyethers by cationic ring opening polymerization is outlined in Scheme 3. Contrary to the general consent, LC polyethers were available almost twenty years before LC polyesters where synthesized. Nevertheless, it took exactly thirty years to **realize** that the polymers from



Scheme 3: Synthesis of LC polyethers by cationic ring opening polymerization and copolymerization of bridged bicyclic ethers.

Scheme 3 exhibit liquid crystallinity[21,22]. Both the cationic homopolymerization of the endo- and exo-2-methyl-7-oxabicyclo [2.2.1] heptane and 7-oxabicyclo [2.2.1] heptane, as well as the copolymerization of the last one with tetrahydrofurane and/or ethylene oxide were first reported at the ACS meeting from Dallas in April 1956[23] and published in 1960[24]. Subsequently, the cationic polymerization of these and other atom-bridged bicyclic ethers, was extensively investigated by several research groups[25] and the study of their polymerization stereochemistry became the classic experiment demonstrating the $S_N2$ mechanism of cationic ring opening polymerization of cyclic ethers[26]. This experiment is also important in explaining the role of constitutional isomerism on phase transitions, and it will be briefly described here. According to the $S_N2$ propagation mechanism, one of the two α-carbon atoms ($C_1$ and $C_4$) of the cyclic oxonium should undergo a Walden inversion to produce the polyether in which the two ether groups at $C_1$ and $C_4$ of a cyclohexane ring are trans to each other. As illustrated by Scheme 3, when the 2-methyl group is in the endo position, the attack on $C_1$ is sterically prohibited and the resulted polyether has all the methyl groups in equatorial positions. In the case of the exo isomer, both the attack at $C_1$ and $C_4$ are allowed, and the resulting polyether is a copolymer containing axial and equatorial methyl groups. It is essential to mention that the constitutional isomeric copolymer obtained from the exo isomer leads to melting transitions which are constantly lower with about 75-100° C than of the corresponding polymer obtained from the endo monomer, i.e., $T_{m(endo)}=257° C$, $T_{m(exo)}= 188°C$, while the melting point of the corresponding unsubstituted polymer is 450° C. The constitutional isomerism affects in a similar way the polymer solubility, i.e. while poly(endo) dissolves only in m-cresol, poly(exo) is soluble in conventional solvents like chloroform and tetrahydrofurane.

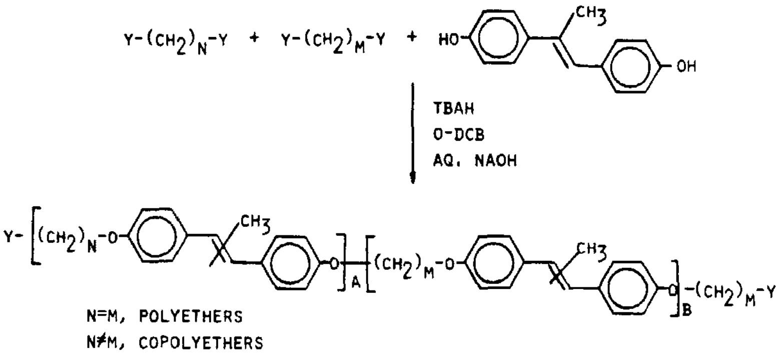
This brief and qualitative discussion of microstructural influences (i.e., constitutional and configurational isomerism) on phase transitions, has certainly pointed out that they have to be very carefully considered when quantitative information on phase transitions are considered. Therefore, in the following chapter some basic molecular-weight microstructure-phase transition relationships in LC polymers and copolymers will be discussed on a very simple polyether system based on 4,4'-dihydroxy-α-methylstilbene and 2,6-dibromoalkanes.

## COPOLYMER COMPOSITION-PHASE TRANSITIONS RELATIONSHIP

As has been qualitatively discussed in the previous chapter, copolymers based on monomer pairs which exhibit constitutional and/or conformational isomerism exhibit completely different phase transitions from those of the parent homopolymers. Quantitative information on this topic are not yet available, and therefore we would restrict ourselves on discussing a simple copolyether system based on 4,4-dihydroxy-$\alpha$-methylstilbene, 1,9-dibromononane and 1,11-dibromoundecane[27]. This experiment received partial encouragement by the conclusions of a recent review on the very few experimental data available on liquid crystalline copolyesters[28]. These are as follows.

Direct comparison of the thermal behaviors of copolymers requires very careful analysis of the experimental data because the sequence distribution and molecular weights, in addition to compositional variations, should be accounted for. However, it may be safe to conclude that copolymers possess wider temperature ranges of mesophase stability, but give rise to less ordered mesophases. In addition, some qualitative ex- experiments led to the following conclusions. A copolymer containing structural units that give rise to nematic homopolymers exhibits nematic mesomorphism[29-31]. At the same time, a copolymer containing structural units that give rise to smectic homopolymers presents smectic mesomorphism[32-34]. In one case, nematic copolymers were obtained from structural units that give rise to isotropic homopolymers[35,36]. An even more interesting experiment has demonstrated that a monotropic mesophase can be transformed into an enantiotropic mesophase by copolymerization[37]. The obvious question we will try to answer is: what kind of behavior shall we expect from a copolyether containing structural units that give rise to smectic and, respectively, nematic homopolymers? To answer this question we first have to eliminate the influence of sequence distribution, then discuss the influence of molecular weight on the phase behavior of each homopolymer in part, and only after, comment on the influence of copolymer composition on phase transitions occurring above the molecular weight where phase transitions are not anymore molecular weight dependent.

A previous experiment from our laboratory has demonstrated that LC copolyethers based on two different spacers and a single mesogenic unit present a random sequence distribution[38]. Therefore, as Scheme 4 shows, although even the homopolymers of 4,4'-dihydroxy-α-



Scheme 4: Syntheses of polyethers and copolyethers on 4,4'-dihydroxy-α-methylstilbene and α,ω-dibromoalkanes.

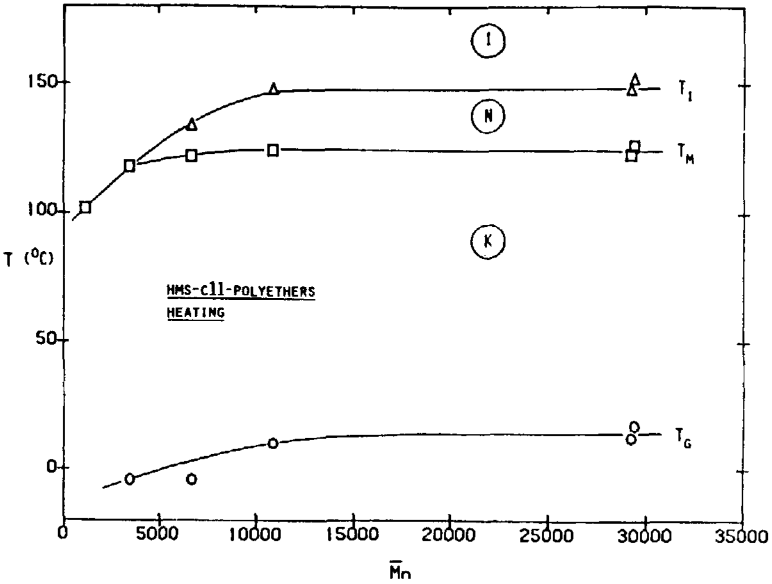


Figure 3: The influence of number average molecular weight ($\overline{M}n$) on the glass transition (Tg), melting (Tm), and isotropization (Ti) temperatures for the HMS-CH polyethers during the heating scan.

methylstilbene (HMS) is in fact a copolymer of the two constitutional isomers of HMS (i.e., methyl group as head or tail) their distribution is random, and therefore depresses the phase transition temperature and enhances the polymer solubility. Both the homopolymers and copolymers outlined in Scheme 4 are soluble in conventional solvents like aromatic and halogenated solvents as well as tetrahydrofurane, allowing molecular weight measurements and conventional solution spectroscopical techniques to be used in their characterization[27]. The following short names are used to describe the homopolymers exhibiting eleven and respectively nine methylene units in the spacer: HMS-C11 and HMS-C9, while HMS-C9/11 is the short name for the corresponding copolymers.

Figures 3 and 4 present the phase transitions as a function of molecular weight of HMS-C11 obtained from the heating and cooling scans. As expected, crystalline transitions are kinetically controlled while mesomorphic transitions are thermodynamically controlled. As a consequence, the lowest molecular weight polymers are only crystalline, the intermediary molecular weight polymers exhibit a monotropic nematic mesophase, while the polymers containing higher molecular weights than

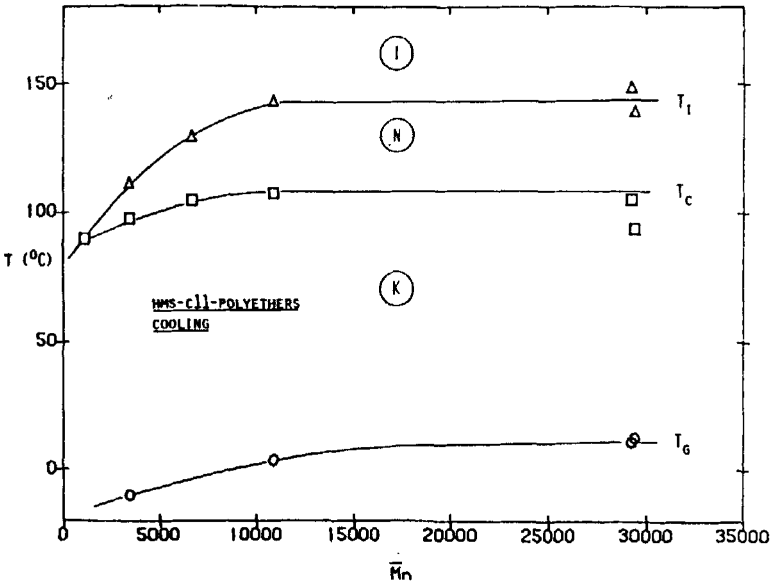


Figure 4: The influence of number average molecular weight ($\bar{M}n$) on the glass transition (Tg), crystallization (Tc), and isotropization (Ti) temperatures for the HMS-C11 polyethers during the cooling scan.

5000 are enantiotropic nematics. Nevertheless, all the phase transitions and their thermodynamic parameters are molecular weight dependent up to at least 12,000 number average molecular weight. Only below this molecular weight, the phase transitions are strongly dependent on the nature of the polymer chain ends[29]. The phase diagram of the HMS-C9 exhibits an almost identical behavior on the heating scan, i.e., the polymer presents a

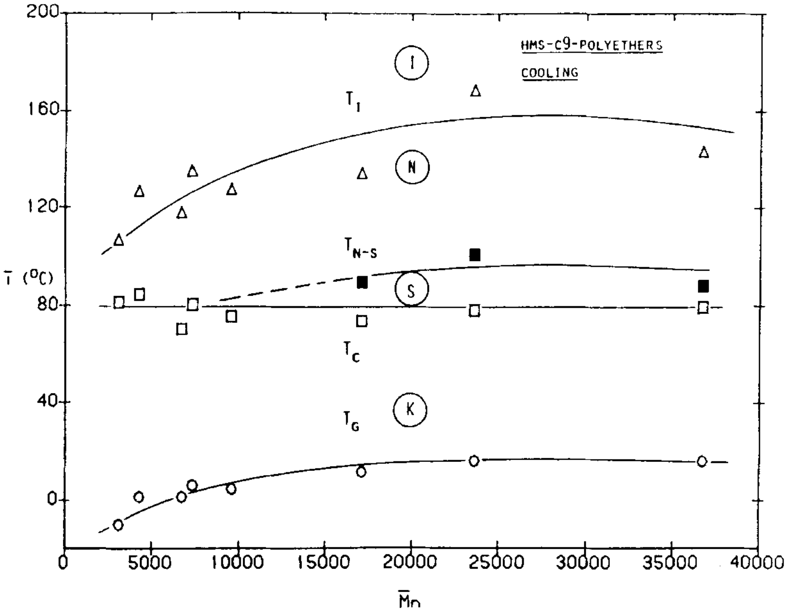


Figure 5: The influence of number average molecular weight ($\bar{M}n$) on the glass transition (Tg), crystallization (Tc), nematic-smectic ($T_{N-S}$), and isotropization (Ti) temperatures for the HMS-C9 polyethers during the cooling scan.

nematic mesophase[27]. The molecular weight-phase transition relationship obtained from cooling scans is shown in Figure 5. Above a certain molecular weight, the polymer exhibits a monotropic smectic mesophase, while the enantiotropic nematic mesophase covers the whole range of molecular weights.

The conclusion of these first experiments is that safe results can be obtained only if the phase diagram of the HMS-C9/11 is made with copolymers having number

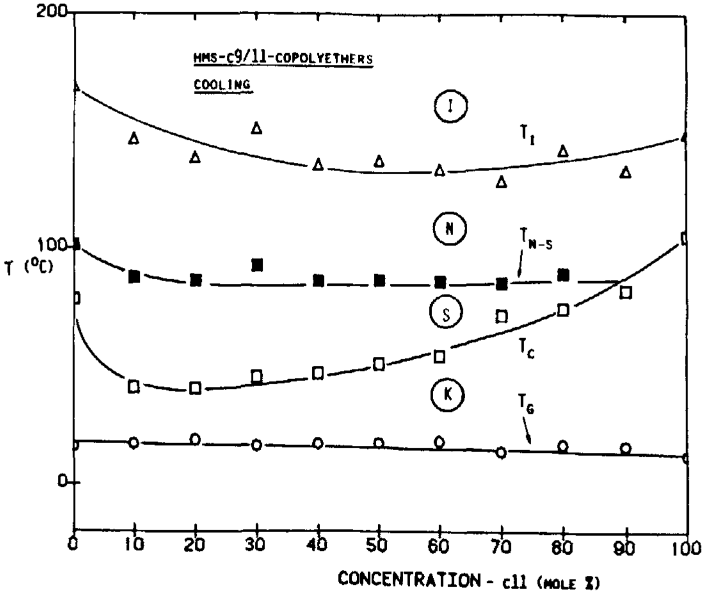


Figure 6: Thermal transitions ($T_g$, Tc, $T_{N-S}$, and Ti) for the HMS-C9/11 copolyethers as a function of copolymer composition on the cooling scan.

average molecular weights above 20,000.

Figure 6 presents the phase diagram of the HMS-C9/11 copolymers obtained from a set of copolymers having number average molecular weights between 30,000 and 40,000. These results were obtained from cooling scans. The figure seems to be self explanatory. The phase diagram of these copolymers resembles the one of the HMS-C9 polyether up to as little as only 20 mole %

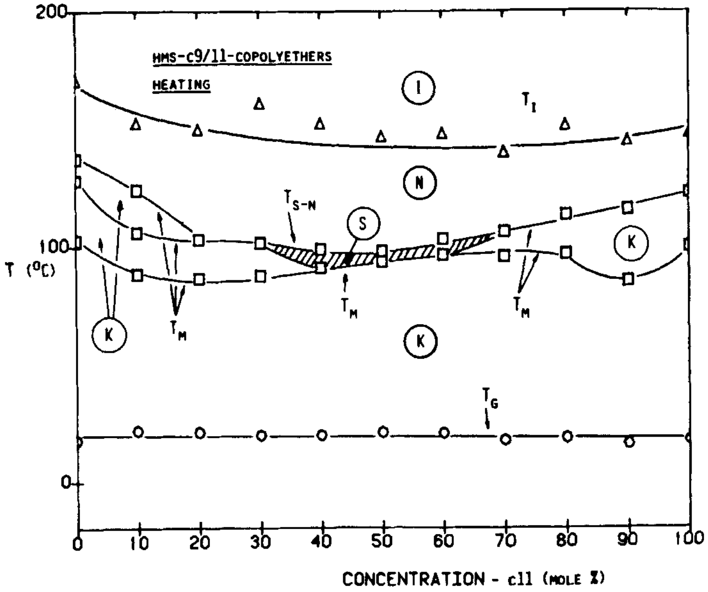


Figure 7: Thermal transitions (Tg, Tm, $T_{N-S}$, and Ti) for the HMS-C9/11 copolyethers as a function of copolymer composition on the heating scan.

C9 in the copolymer. This seems to conclude, that the phase diagram is dictated by the short spacer. The long spacer depresses the crystallization temperature.

Figure 7 presents the phase diagram of HMS-C9/11 on heating. Interesting to observe is that at about 50/50 mole ratio of the two spacers, the monotropic smectic mesophase becomes enantiotropic. In addition, the thermodynamic data for all phase transitions, demonstrates that the degree of order in the mesophase does not decrease by copolymerization[27].

A simplified explanation which is going to be detailed in another paper from these proceedings is as follows[39]. The phase diagram is controlled by the short spacer which is in an all trans extended conformation. The long spacer has a coiled conformation, and as expected decreases the rate of crystallization but not the degree of order in either crystalline or mesomorphic phase. If this structural model is general, it opens a large variety of possible preparative variations since in this case the coiled spacer can accommodate functional groups. Additional work to support and generalize this concept is performed in cooperation with Prof. A. Keller's group.

## MISCIBILITY BETWEEN SIDE GROUPS AND MAIN CHAIN: DOES IT REPRESENT AN ADDITIONAL PARAMETER TO BE CONSIDERED BY THE SPACER CONCEPT?

Since Ringsdorf *et al.*[8,9] have advanced the spacer concept to decouple the motion of the side groups from that of the main chain, thermotropic side chain LCP have received considerable research interest both from practical and fundamental point of view[1,2]. Subsequent work by Ringsdorf *et al.*[10-12] has shown that complete decoupling does not occur although the degree of decoupling increases with the spacer length[11].

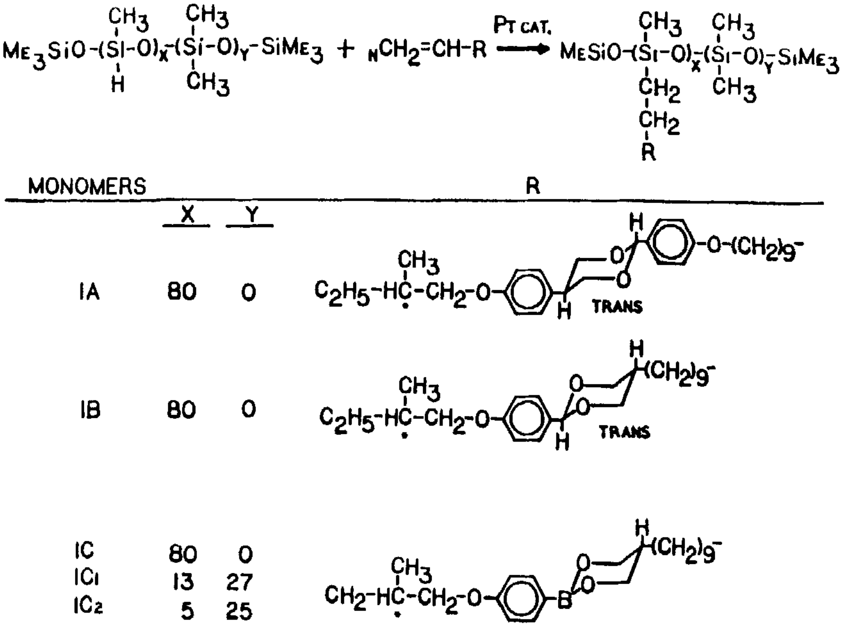
Several recent publications have suggested that not only the nature and length of the flexible spacer, but also the nature of the polymer backbone influences the range of thermal stability of the mesophase, and that the broadest thermal stability of the mesophase is always obtained with the most flexible backbones[40-48].

We assume that the nature of the polymer backbone plays a more important role than previously considered in achieving a highly decoupled side chain LCP. The enhanced thermal stability of the mesophase and the increased isotropization temperature exhibited by polymers presenting flexible backbones can be associated with a high degree of freedom of the side groups. This might be related not only to the mobility of the polymer backbone, but also to its miscibility with the side groups[48]. This statement can be more clearly understood if we make a comparison between side chain LCP and graft copolymers. When the graft and the backbone are miscible, the overall properties of the graft copolymer are weight averaged. When the graft and the backbone are immiscible, the graft copolymer exhibits a micro-phase separated mesophology and the graft copolymer presents synergistic properties exhibited by the individual graft and backbone segments. The micro-phase separated morphology of a graft copolymer when transplanted to a side chain LCP in our opinion should give rise to a highly decoupled side chain LCP. Therefore, it is not only the spacer length which controls the degree of decoupling, but also the miscibility between the side chains and the polymer backbone.

Recently we have reported the first examples of biphasic, i.e., micro-phase separated side chain LCP[45-47,49]. These polymers exhibit two glass transition temperatures, i.e. one due to the independent motion of the main chain, and the other due to the cooperative but independent motion of the side groups. These side chain LCP might represent the first examples of highly decoupled side chain LCP. One of the most important parameters in achieving such a micro-phase separated LCP consisted in the use of the very long spaces and mesogenic units which did not undergo side chain crystallization. We have investigated three different types of side chain LC copolymers as possible candidates for the synthesis of polymers which do not undergo side chain crystallization. The first class is based on monomer pairs containing mesogenic units which exhibit constitutional or structural isomerism[48,50].

The second type of copolymer is based on monomers containing a mesogenic unit which exhibits conformational isomerism like for example benzyl ethers, diphenyl ethanes, trans 2,5- disubstituted-1,3-dioxanes or 2,5-disubstituted-1,3,2-dioxaborinanes[45-47,51], while the last type of copolymer is based on monomer pairs containing mesogenic units which exhibit both constitutional and conformational isomerism[45]. Although all three procedures were quite successful, the second one seems to be the most convenient from the preparative point of view. Since the conformational isomers of these mesogenic groups are in a dynamic equilibrium, a mixture of conformational isomers has a lower tendency towards crystallization than each of the isomers in part, and therefore, side chain crystallization could be avoided in many cases.

Two representative examples are going to be briefly described here. Scheme 5 outlines the synthesis of three chiral smectic LC polysiloxanes and of a series of copolysiloxanes. Their detailed synthesis and and characterization is described elsewhere[47], and for the purpose of this discussion we will not consider their high temperature mesomorphic transitions. None of the homopolymers or copolymers exhibit side chain crystalliza-



Scheme 5: Synthesis of polysiloxanes and copolysiloxanes containing IA, IB and IC side groups.

tion. Nevertheless, since the weight fraction of the side groups is very high, it is difficult only from DSC experiments to ascertain for their micro-phase separated morphology. However, in copolysiloxanes $IC_1$ and $IC_2$ the weight fraction of the side groups is about 50% of the overall weight of the polymer. The DSC traces of these two copolymers are presented as thermograms A and B from Figure 8, together with representative thermograms exhibited by a polydimethylsiloxane (curve C) and a

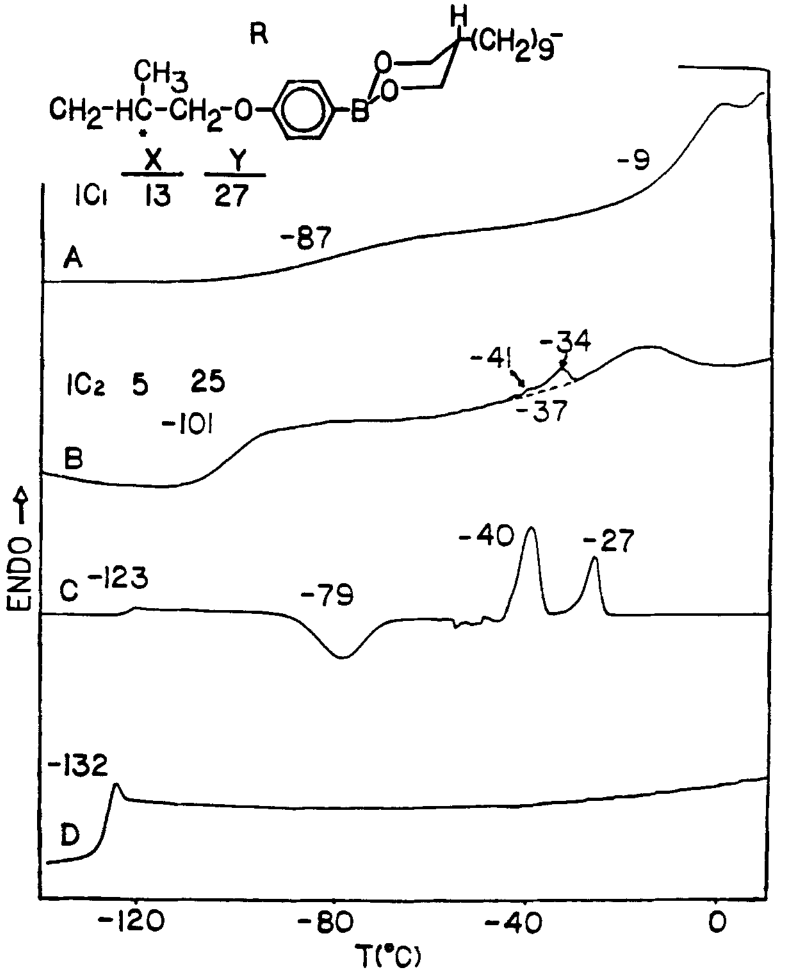


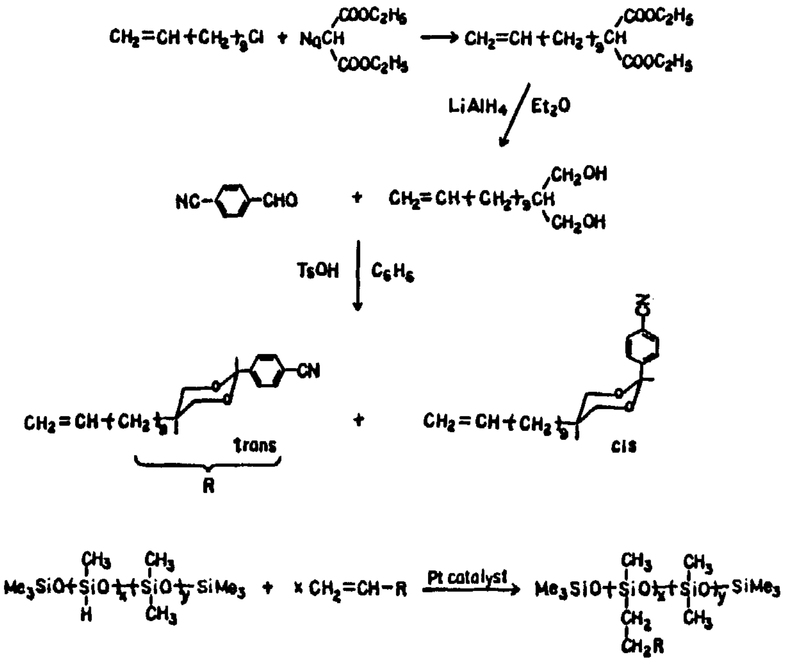
Figure 8: DSC thermograms (20°C/min) of:

A) second heating scan of polymer IC1 from Scheme 5:

B) second heating scan of polymer IC2 from Scheme 5;

C) second heating scan of polydimethylsiloxane, $\bar{M}n$ = 5600;

D) second heating scan of the poly[(30-35%)-hydrogenmethyl-(65-70%)-dimethyl-siloxane], $\bar{M}n$ = 2000-2100.



Scheme 6: Synthesis of polysiloxanes and copolysiloxanes containing trans 5-n-undecanyl-2-(4-cyanophenyl)-1,3-dioxane side groups.

starting poly(hydrogenmethyl-dimethylsiloxane) material (curve D). Both LC copolymers exhibit two glass transition temperatures. The change in the heat capacity at the Tg is proportional to the weight fraction of the polymer backbone for the low temperature Tg, and to the weight fraction of the side groups for the high temperature Tg. Therefore, the low temperature Tg is due to the independent motion of the main chain, while the high temperature Tg is due to the cooperative but independent motion of the side groups. It is interesting to observe that in the case of copolymer $IC_2$, the polymer backbone crystallizes and exhibits two melting transitions (at -41° and -34° C) which overlap the Tg of the side groups. This behavior is definitively demonstrating that the motion of the side groups is independent of the motion of the main chain.

Scheme 6 illustrates the synthesis of an additional example of LC copolysiloxane exhibiting two glass transition temperatures, while Table I presents the thermal transitions of the polysiloxanes and copolysiloxanes containing 5-n-undecanyl-2-(4-cyanophenyl)-1,3-dioxane side groups[46]. As in the case of the previously discussed example, all the copolysiloxanes synthesized as outlined in Scheme 6, exhibit two glass transition temperatures, the lowest due to the independent motion of the main chain, the highest due to the cooperative but independent motion of the side groups.

These results represent a strong evidence for a well defined micro-phase separated morphology, and demonstrate that in biphasic LC polymers, the mobility of the LC domains is independent of the mobility of the

TABLE I: THERMAL TRANSITIONS AND THERMODYNAMIC PARAMETERS OF POLYSILOXANES FROM SCHEME 6

| POLYMERS | | | THERMAL TRANSITIONS, (°C) AND THERMODYNAMIC PARAMETERS, ΔH(KCAL/MRU*),ΔS(CAL/MRU*,°K) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | HEATING | | | | | | | | COOLING | | |
| NO. | X | Y** | $T_{G1}$ | $T_C$ | $T_{M1}$ | $T_{M2}$ | $T_{G2}$ | $T_I$ | $\Delta H_I$ | $\Delta S_I$ | $T_I$ | $\Delta H_I$ | $\Delta S_I$ |
| 1 | 0 | 80 | -123 | -79 | -40 | -26 | -- | -- | -- | -- | -- | -- | -- |
| 2*** | 10 | 20 | -126 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 3*** | 5 | 25 | -127 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 4 | 80 | 0 | -- | -- | -- | -- | -10 | 149 | 0.57 | 1.35 | 140 | 0.56 | 1.36 |
| 5 | 38 | 0 | -- | -- | -- | -- | -10 | 135 | 0.52 | 1.27 | 128 | 0.54 | 1.35 |
| 6 | 10 | 20 | -100 | -- | -- | -- | -39 | 66 | 0.67 | 1.98 | 64 | 0.67 | 1.99 |
| 7 | 5 | 25 | -105 | -- | -- | -- | -58 | -- | -- | -- | -- | -- | -- |

* MRU = MOLE OF REPEAT UNITS,CONSISTING OF MESOGENIC UNIT AND TEN METHYLENIC UNITS.

** X AND Y ACCORDING TO SCHEME 6.

*** POLY(X-HYDROGENMETHYL-Y-DIMETHYLSILOXANE)

backbone domains, although they are chemically interconnected. This is contrary to the behavior of LCP exhibiting a single phase morphology.

It is certain that the mesomorphic behavior of the side chain LCP should be strongly affected by the weight ratio of the domains, domain size, interfacial miscibility, and all the other particularities which dictate the overall properties of the phase separated polymeric systems.

These results are raising a number of fundamental questions concerning the behavior of biphasic versus monophasic side chain liquid crystalline polymers.

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