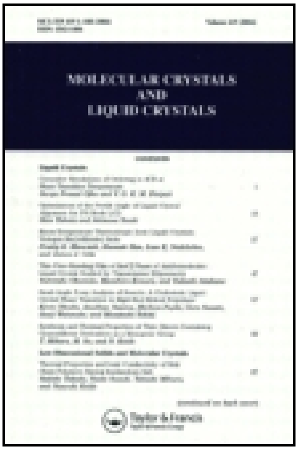

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Synthesis and Characterization of Thermotropic Polyethers and Copolyethers Based on 4,4′-dihydroxy-α-methylstilbene and Flexible Spacers Containing Odd Numbers of Methylene Units

V. Percec [a] , K. Asami [a] , D. Tomazos [a] , J. L. Feijoo [b] , G. Ungar [b] & A. Keller [b]

[a] Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH, 44106, U.S.A.

[b] H. H. Willis Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, U.K.

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Synthesis and Characterization of Thermotropic Polyethers and Copolyethers Based on 4,4′-dihydroxy-α-methylstilbene and Flexible Spacers Containing Odd Numbers of Methylene Units

V. PERCEC, K. ASAMI and D. TOMAZOS

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, U.S.A.

and

J. L. FEIJOO, G. UNGAR and A. KELLER

H. H. Willis Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, U.K.

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This paper describes the synthesis and characterization of thermotropic polyethers and copolyethers based on 4,4′-dihydroxy-α-methylstilbene (HMS) and flexible spacers containing odd number of methylene units [i.e., HMS-X/Y(A/B), where X is the number of methylene units in one of the spacers, Y is the number of methylene units in the other spacer, and A/B refers to the molar ratio of the two spacers]. The polyethers HMS-X are binary copolymers containing structural units derived from the two constitutional isomers of HMS and the flexible spacer. The binary copolymers HMS-X/Y(A/B) contain four structural units derived from combinations of the two constitutional isomers of HMS and the two flexible spacers. The following polymers and copolymers were synthesized and characterized: HMS-5, HMS-7, HMS-9, HMS-11, HMS-13(A/B), HMS-5/7(A/B), HMS-5/9(A/B), HMS-5/11(A/B), HMS-7/9(A/B), HMS-9/11(A/B), and HMS-9/13(A/B). All polymers had number average molecular weights higher than 15,000 and exhibited an enantiotropic nematic mesophase and several crystalline phases. Both the crystalline and the liquid crystalline phases are kinetically controlled i.e., their thermal transition temperatures and associated enthalpy changes are dependent on the heating rate and thermal history of the sample. These results led to the conclusion that for high molecular weight semi-flexible liquid crystalline polymers non-equilibrium states exist both in the liquid crystalline and crystalline phases. Quasi-equilibrium nematic-isotropic transition temperatures and enthalpy changes were obtained either from the first heating scan or after suitable annealing of the polymer sample.

INTRODUCTION

In several previous publications from our laboratories we have reported preliminary results on the synthesis and characterization of liquid crystalline polyethers and copolyethers based on 4,4′-dihydroxy-α-methylstilbene (HMS) and α,ω-dibromoalkanes containing various numbers of methylene units. In a first communication we have reported the synthesis and phase behavior of polyethers based on HMS and α,ω-dibromoalkanes containing from three to eight methylene units.[1] Subsequent experiments have investigated the influence of molar ratio between 1,5-dibromopentane and 1,7-dibromoheptane on the phase behavior of the copolymers with HMS.[2] The influence of the polymer molecular weight on the phase transition temperatures and their thermodynamic parameters was investigated for a copolymer based on HMS and a 1/1 molar ratio between 1,5-dibromopentane and 1,7-dibromoheptane.[3] These experiments have demonstrated that for polymers with number average molecular weights lower than 12,000 both thermal transition temperatures and their corresponding thermodynamic parameters are molecular weight dependent.[3a] These results agree with those reported previously with liquid crystalline polyesters.[3b] Therefore, the transitions of polyethers and copolyethers investigated previously were still molecular weight dependent.[1,2] In addition, within the range of low molecular weights, phase transition temperatures and thermodynamic parameters are also dependent on the nature of the polymer chain ends.[2a,b] A more comprehensive investigation was performed on polyethers based on 1,9-dibromononane and 1,11-dibromoundecane and HMS, respectively.[4] These experiments have demonstrated that the polymer molecular weight does influence both the transition temperature and its thermodynamic parameters as well as the relative thermodynamic stability of the mesophase with respect to the stability of the crystalline phase. Therefore, upon increasing the molecular weight of the polymer the virtual or monotropic mesophase exhibited by the oligomer may be transformed into an enantiotropic mesophase.[4] Subsequently, the phase behavior of copolymers based on 1,9-dibromononane, 1,11-dibromoundecane and HMS was investigated for copolymer molecular weights which are higher than $M_n = 15{,}000$. These last experiments have demonstrated that copolymerization can also transform a monotropic or virtual mesophase of the homopolymer into an enantiotropic one.[4,5]

More recently, upon investigating different crystalline phases of these polymers,[6] it has been discovered that different thermal treatments affect both the temperature and the heat of isotropization.[7] Based on these results, it has been concluded that for high molecular weight polymers non-equilibrium states exist both in the liquid crystalline[6] and isotropic[8,9] states.

In an attempt to accomplish a comprehensive understanding of these series of polyethers, we have investigated the synthesis and the thermal characterization of polymers based on HMS and α,ω-dibromoalkanes containing different odd and even number of carbon atoms. The influence of thermal history of the sample on the thermal transition temperatures and their thermodynamic parameters will be critically considered. This paper describes the synthesis and characterization of polyethers and copolyethers based on HMS and α,ω-dibromoalkanes containing odd numbers of methylene units ranging from 1,5-dibromopentane to 1,13-dibromotridecane.

EXPERIMENTAL

Materials

1,5-Dibromopentane (97% from Aldrich) was fractionated by vacuum distillation. 1,7-Dibromoheptane (97%), 1,9-dibromononane (97%) (both from Aldrich) were used as received. 1,13-Dibromotridecane was synthesized and characterized as described in a previous publication.[10] Tetrabutylammonium hydrogen sulfate (TBAH) (97%) and *o*-dichlorobenzene (99%) (both from Aldrich) were used as received.

Synthesis of 4,4'-Dihydroxy-α-methylstilbene (HMS)

HMS was prepared by a method which represents a modification of a previously reported procedure.[3] Although the yield in the present synthesis is lower than in the previous one, the new method avoids the purification of HMS by a combination of Soxhlet extraction and column chromatography. A general procedure is as follows. To a mechanically stirred mixture of freshly distilled phenol (118 g, 1.26 mol) and freshly distilled chloroacetone (58 g, 0.627 mol) cooled in a methanol-dry ice bath maintained at −10 to −15°C, concentrated sulfuric acid (29 g, 0.296 mol) was added dropwise over 1 hr. The reaction mixture was stirred at this temperature for two additional hours. The orange-red pasty mass was treated with a large excess of ice-cold water/ethanol (10/1, vol/vol) mixture and was mechanically stirred for 24 hrs. The precipitated solid was filtered and recrystallized six times from an ethanol/water (6/4, vol/vol) solution. The resulting HMS has a purity of 99.0–99.9% (HPLC). Yield, 8.3 g (5.9%). mp = 185°C (DSC, 20°C/min). ^{1}H-NMR (DMSO-d_6, TMS, δ, ppm): 2.20 (—C$\underline{H}_3$, *s*), 6.70 (=C$\underline{H}$—, *s*), 6.85 (4 aromatic protons, *o* to OH, *d*), 7.25 (2 aromatic protons, *o* to α-CH_3, *d*), 7.40 (2 aromatic protons, *o* to =CH—, *d*).

Synthesis of Polyethers and Copolyethers

Conventional liquid-liquid two phase (organic solvent-aqueous NaOH solution) phase transfer catalyzed polymerization conditions were used for the synthesis of polyethers and copolyethers.[3,4] Polymerizations were carried out under nitrogen atmosphere at 80°C in *o*-dichlorobenzene-10N NaOH water solution. The molar ratio of nucleophilic monomer to electrophilic monomers was in every case 1.0/1.0. The amount of HMS (0.226 g, 1 mmol), *o*-dichlorobenzene (2.5 ml) and NaOH (10N, 2.0 ml) was maintained constant for all polymerizations and copolymerizations. In order to obtain reproducible results and polymers with high molecular weights it is essential that these experiments are performed in a 25 ml single-neck flask (No. 19/22 from Ace Glass) with a magnetic stirring bar of 7.9 mm diameter and 22.2 mm length (Spinbar from Sargent-Welch). The reaction mixture was stirred at 1000 rpm with a magnetic stirrer (Tekmar RCT-S21) for six hrs. An example is described below. To a mixture of HMS (0.226 g, 1 mmol), 1,5-dibromopentane (0.115 g, 0.5 mmol), 1,7-dibromoheptane (0.129 g, 0.5 mmol) and 2.5 ml of *o*-dichlorobenzene were added 0.068 g (0.2 mmol) TBAH and 2.0 ml of 10N aqueous solution of NaOH. After 6 hrs of reaction at 80°C, the organic and aqueous layers were diluted with *o*-dichlorobenzene and water, respectively, and the aqueous layer was removed. The organic layer was washed with water and dilute hydrochloric acid, and finally with water again. The polymer was separated by the precipitation of the polymer solution into methanol to obtain a white fibrous precipitate. All polymers were purified by filtering their chloroform solution followed by one precipitation into acetone and one into methanol. Yield, 0.246 g (84%). M_n = 21,600, M_w = 48,500; M_w/M_n = 2.20. Yields were about 90% in all cases.

Over the entire manuscript the polyethers will be designated HMS-X, where X is the number of methylene units in the spacer. Similarly, binary copolyethers will be designated HMS-X/Y(A/B), where X is the number of methylene units in one of the spacers, Y is the number of methylene units in the other spacer, and A/B refers to the molar ratio of the two spacers.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC). High pressure liquid chromatography (HPLC) and GPC analyses were carried out with a Perkin-Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler, and Sigma 15 data station. The measurements were made using a UV detector, THF as solvent (1 ml/min; 40°C), a set of PL gel columns of 10^2, 5×10^2, 10^3, 10^4, and 10^5 A and a calibration plot constructed with polystyrene standards. A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS Data Station model 3600, was used to determine the thermal transitions. Heating and cooling rates were 20°C/min in all cases. First order transitions (crystalline-crystalline, crystalline-liquid crystalline, liquid crystalline-isotropic, etc.) were read at the maximum of the endothermic or exothermic peaks. Glass transition temperatures (T_g) were read at the middle of the change in heat capacity. Thermal transition temperatures and their corresponding enthalpy changes are depending on the heating scan they are collected from. Therefore, within the entire manuscript we will refer to this information. A Carl-Zeiss optical polarized microscope (magnification: 100X) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[11,12]

RESULTS AND DISCUSSION

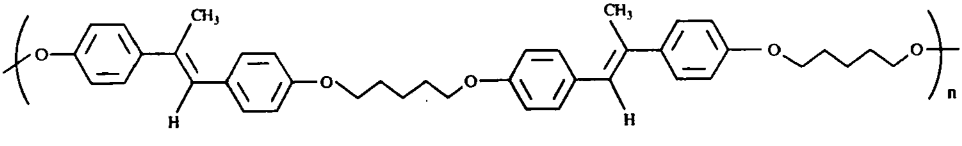
Liquid Crystal Polyethers versus Liquid Crystal Polyesters

Progress in the field of liquid crystalline polymers requires substantial improvements in our ability to tailor-make well defined main chain and side chain liquid crystalline polymers. The relationship structure-phase transition properties in main chain liquid crystalline polymers is one of the multiple problems which continue to demand additional and systematic investigations.

The most reliable and simple synthetic technique which is used to manipulate the structure of polymers, and the least understood in the field of liquid crystalline polymers is copolymerization.[14–25] With very few exceptions,[5] main chain liquid crystalline polymers and copolymers are synthesized by step polymerizations which are based on reversible or irreversible reactions. In contrast to chain copolymerizations, step copolymerizations performed in a homogeneous phase at high conversion and with a stoichiometric radio between comonomers always lead to copolymer compositions which are identical to comonomer feed. This implies that the compositional heterogeneity of the copolymers obtained by step reactions is lower than that of copolymers synthesized by chain copolymerizations whose copolymer composition is conversion dependent. However, again in contrast to chain copolymerizations, in step copolymerizations the copolymer's sequence distribution can be either kinetically (in irreversible copolymerizations) or thermodynamically (in reversible copolymerizations) determined. In reversible step copolymerizations, the kinetic control over microstructure is lost in the early stages of the reaction and the sequence distribution is thermodynamically controlled. In other words, the copolymer microstructure is determined by redistribution reactions. Redistribution reactions take place either during the polymerization process or after if the polymer is annealed. The driving force toward a certain copolymer microstructure is provided by the nature of the phase in which copolymerization or thermal annealing is performed. The copolymer sequence distribution[18,19,22–25] and the configuration of the structural units[26,27] are both determined by the type of phase (isotropic, liquid crystalline or crystalline) in which copolymerization or the copolymer reorganization reaction is performed. Microheterogeneous copolymerization reactions complicate the control of the copolymer's microstructure since the comonomers' concentration around the growing chain is determined by the miscibility and/or the association between the growing chain and the monomers. The concept that a growing active chain can control its own environment during copolymerization was explained based on the "bootstrap model" and its implications were recently reviewed for the case of chain copolymerizations.[28] Some of the most recent examples of "bootstrap effects" were observed in the radical copolymerization of macromonomers,[29,30] in the synthesis of block copolymers from immiscible amorphous segments,[31,32] and in the synthesis of ternary copolymers from monomers which can give rise to amorphous and liquid crystalline structural units by reversible copolymerization reactions.[33]

The situation is less complicated in the case of irreversible step copolymerization reactions performed in a homogeneous phase. On this account, our investigations on the elucidation of copolymer composition and on mesomorphic phase transitions are performed with liquid crystalline copolyethers. These copolymers are synthesized by an irreversible S_N2 two phase (aqueous inorganic base-organic solvent) phase transfer catalyzed polyetherification. Although these polymerizations are performed in a heterogeneous system, the reaction takes place in the organic phase, and therefore, from a kinetic point of view,[34] they are treated as one phase solution polymerizations.

In conclusion, the main advantages of using liquid crystalline polyethers and copolyethers for fundamental investigations consist in their "thermally stable" microstructure and molecular weight, and higher compositional homogeneity. In addition, since ether bonds are more flexible than ester bonds they enhance polymer solubility and lower phase transition temperatures, providing samples which can be investigated at lower temperatures. For the case of liquid crystalline polyesters and copolyesters, both their microstructure and molecular weight are changing very rapidly during thermal annealing especially when annealing is performed in the isotropic or liquid crystalline phase. Since the microstructure of copolyethers is kinetically determined, it allows us to estimate in advance the possible sequence distribution of a certain polymer. For example, we could assume that homopolymers based on HMS and α,ω-dibromoalkanes are in fact copolymers containing two constitutional isomeric structural units of HMS. The first one has the methyl group in the α-position (structural unit A), the other in the β-position (structural unit B):



structural unit A structural unit B

These two structural units A and B are almost randomly distributed since the reactivity of the two phenolate groups derived from HMS is similar. This assumption was supported by monoalkylation experiments which showed that the 4- and 4′-hydroxy groups of HMS are alkylated with about equal probability.[35] A random distribution of the constitutional isomeric side groups suppresses crystallization and therefore decreases melting temperatures and increases the polymer solubility. This conclusion was reached by synthesizing side chain liquid crystalline homopolymers based on 4-methoxy-4′-hydroxy-α-methylstilbene[36] and 4-hydroxy-4′-methoxy-α-methylstilbene[37] mesogenic groups and by comparing their thermotropic behavior with that of their corresponding constitutional isomeric copolymers.[38,39] Since constitutional isomeric mesogenic groups based on HMS exhibit almost identical mesomorphism, upon copolymerization mainly their crystallization tendency is suppressed. Therefore, in many cases copolymerization of the two constitutional isomeric mesogens transforms virtual or monotropic mesophases into enantiotropic mesophases.[38,39]

Based on similar assumptions, binary copolyethers of HMS with α,ω-dibromoalkanes lead to ternary copolymers containing the two constitutional isomers of HMS and the two flexible spacers.

Copolymers Based on One Mesogenic Unit and Two or More than Two Flexible Spacers

Before discussing the experimental data it may be instructive to review briefly the phase behavior of liquid crystalline copolymers based on one rigid or flexible rod-like mesogenic unit and two or more than two flexible spacers. Several research groups have performed this experiment with polyesters. Their results tend to lead to the conclusion that copolymerization of two flexible spacers with a mesogenic unit suppresses the crystallization transition temperature and lead to a linear dependence between the isotropization temperature and copolymer composition.[40–44] A series of systematic copolymerization experiments was performed with the flexible mesogen 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and pairs of two flexible spacers containing odd numbers of methylene units,[45,46] even number of methylene units,[47] combinations of odd and even numbers of methylene units,[48,49] and combinations of three[50] and more than three[51] different flexible spacers. The same conclusion was obtained for all these series of experiments. Copolymerization depresses the melting temperature and, subsequently, can transform virtual or monotropic mesophases into enantiotropic mesophases. However, for polymers with molecular weights above the value which influences thermal transition temperatures, identical or isomorphic mesophases of copolymers display both thermal transition temperatures and enthalpy changes which represent weight averaged values of the corresponding parameters of parent homopolymers. These results demonstrate that the structural units of copolymers are isomorphic in the liquid crystalline phase, but not in the crystalline phase.[52] These experiments demonstrate that copolymerization does not represent only one of the most powerful techniques available to manipulate polymer phase transitions, but also becomes the only available synthetic tool which can be used to determine virtual mesomorphic phase transitions and thermodynamic parameters of homopolymers. The second approach to this problem is based on polymer mixtures. However, we have demonstrated that this approach is more limited than copolymerization.[52] The dependences between phase transition temperatures, copolymer composition and molecular weight were recently explained based on thermodynamics.[53,54]

Copolyethers based on HMS and Pairs of α,ω-dibromoalkanes Containing Odd Numbers of Methylene Units

The following homopolymers and series of copolymers will be discussed: HMS-5, HMS-7, HMS-9, HMS-13, HMS-5/7, HMS-5/9, HMS-5/11, HMS-7/9, HMS-9/11, and HMS-9/13. Attempts were made to synthesize polymer samples with number average molecular weights above M_n = 15,000 in order to eliminate molecular weight influences on thermal transitions.[3,4,7]

Let us begin our discussion with the reinvestigation of the copolymer system HMS-9/11 which was presented in a previous publication.[3] Previously, all thermal characterization results of HMS-9/11 copolymers obtained by DSC experiments were collected from second or subsequent heating and cooling scans.[3] This is a general trend followed by the entire polymer liquid crystal research community in order to avoid the irreproducibility of the first DSC heating scan. The observation of the nonequilibrium state of the mesomorphic phase of polymers with high molecular weight prompted us to investigate more carefully the first DSC heating scan by comparison with the subsequent scans. These experiments were performed both for the case of side chain[37,55] and main chain[45,46] liquid crystalline polymers. In both cases, the general conclusion obtained was that the first DSC heating scan which is considered irreproducible and is therefore disregarded by most investigators, corresponds almost to the equilibrium situation.[46,55]

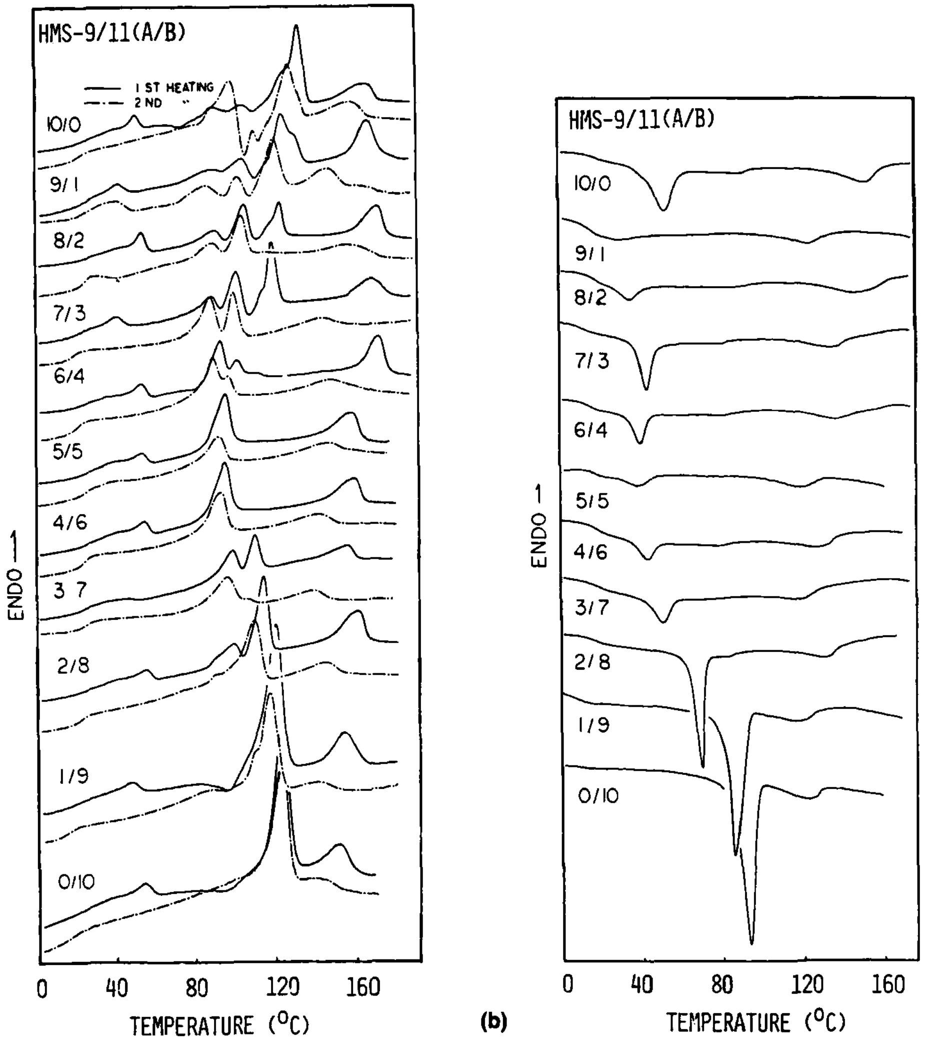


FIGURE 1 a) First (-) and second (- · - ·) DSC (20°C/min) heating scans of HMS-9/11(A/B). b) First cooling DSC (20°C/min) scans of HMS-9/11(A/B).

This first DSC scan is performed on the polymer sample which was separated from solution by precipitation from a nonsolvent followed by drying. The second heating scan differs from the first one especially in regard to phase transitions which are kinetically controlled (i.e., crystalline, and for high molecular weight polymers also liquid crystalline). The first heating scan can be reproduced only after careful annealing of the same DSC sample pan under suitable thermal conditions.[46] Figure 1a presents first and second DSC heating scans for the series of copolyethers HMS-9/11. Thermal transition temperatures obtained from different heating and cooling scans, and molecular weights are summarized in Table I. With the exception of HMS-11 and HMS-9/11 (1/9) all other copolymers have number average molecular weights above M_n = 28,000. Therefore, it is fair to compare their phase transition

TABLE I

Characterization of polyethers and copolyethers based on HMS, 1,9-dibromononane and 1,11-dibromoundecane [HMS-9/11(A/B). Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line, *g* = glassy, *k* = crystalline, *n* = nematic, *x* = unknown phase.

HMS-9/11(A/B)	M_n	M_w/M_n	Thermal transitions (°C), and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	23500	2.75	g 26 k 135 n 167(0.53) i g 21 k 129 n 159(0.47) i	i 151(0.66) n 89 x 57 k 18 g
9/1	34900	2.05	g 19 k 133 n 164(0.79) i g 22 k 85 n 139(0.39) i	i 124(0.40) n 28 k 14 g
8/2	28800	2.69	g 27 k 122 n 170(0.81) i g 24 k 102 n 155(0.47) i	i 148(0.65) n 86(0.13) x 34 k 18 g
7/3	28400	2.69	g 20 k 121 n 170 (0.65) i g 19 k 101 n 142(0.54) i	i 135(0.53) n 80(0.04) x 43 k 12 g
6/4	33300	2.12	g 25 k 111 n 172(0.82) i g 21 k 97 n 148(0.69) i	i 136(0.58) n 82(0.12) x 39 k 13 g
5/5	38400	2.05	g 27 k 94 n 157(0.90) i g 25 k 91 n 143(0.35) i	i 122(0.45) n 76(0.08) x 41 k 16 g
4/6	28700	1.45	g 25 k 95 n 159(0.85) i g 25 k 92 n 139(0.46) i	i 127(0.48) n 79(0.08) x 42 k 16 g
3/7	41700	2.51	g 15 k 110 n 157 (0.89) i g 25 k 105 n 138(0.41) i	i 120(0.48) n 75(0.04) x 50 k 17 g
2/8	29800	2.42	g 31 k 113 n 159(0.96) i g 22 k 108 n 143(0.50) i	i 131(0.60) n 83(0.03) x 68 k 15 g
1/9	12500	1.97	g 22 k 121 n 154(0.88) i g 15 k 118 n 141(0.20) i	i 120(0.40) n 89 k 7 g
0/10	18900	2.04	g 23 k 126 n 153(0.84) i g 15 k 122 n 143(0.35) i	i 124(0.44) n 94 k 9 g

temperatures for different copolymer compositions. A first inspection of Figure 1a tells us that isotropization temperatures obtained from the first heating scans are higher than those obtained from the second heating scans. At the same time the isotropization peaks from first scans are sharper than those of the second scans. Heating scans subsequent to first heating scans are all identical. All cooling scans are also identical (Figure 1b). Therefore, Table I summarizes glass transition temperatures, the highest melting temperatures prior to the nematic phase, and the isotropization temperatures determined from first and second heating scans and from first cooling scans. A second inspection of Figure 1a reveals that the number of melting endotherms obtained during the second heating scan is lower than that obtained from the first heating scan. The melting endotherm from just above the glass transition is always missing in the second heating scan. Nevertheless, upon

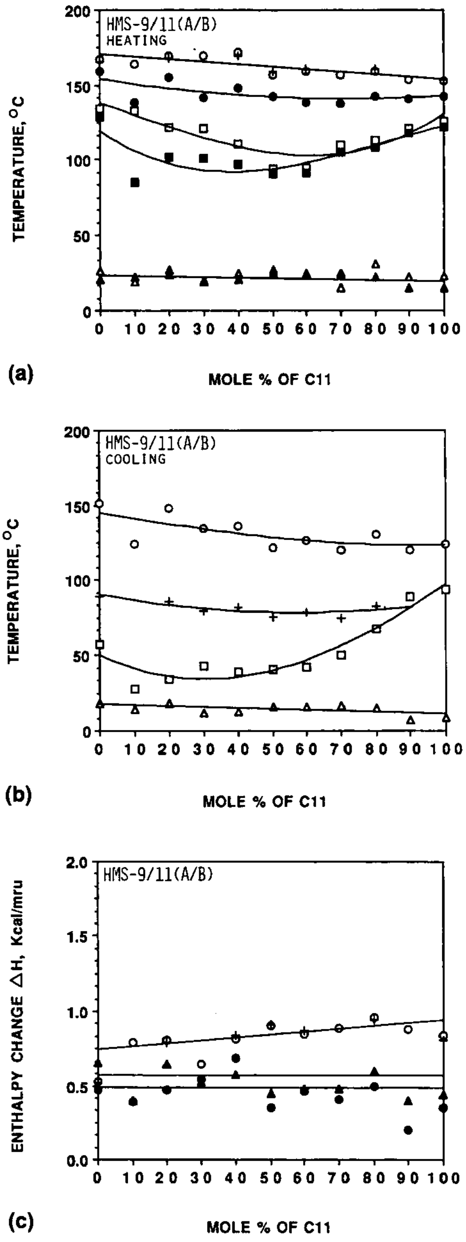


FIGURE 2 a) The dependence between thermal transition temperatures obtained from first and second heating scans and HMS-9/11(A/B) copolymer composition. T_g (Δ first scan, ▲ second scan, T_m (□ first scan, ■ second scan), T_{n-i} (○ first scan, ● second scan, + first scan after annealing at 80°C for 5 hrs. b) The dependence between thermal transition temperatures obtained from first cooling scan and HMS-9/11(A/B) copolymer composition. T_g (Δ), T_{s-k} or T_{n-k} (□), T_{n-s} (+), T_{i-n} (○). c) The dependence between the enthalpy change associated with the isotropization transition (ΔH_i) and HMS-9/11(A/B) copolymer composition. ○ first heating scan, ● second heating scan, ▲cooling scan, + first heating scan after annealing at 80°C for 5 hrs.

TABLE II

Characterization of polyethers and copolyethers based on HMS, 1,5-dibromopentane and 1,7-dibromoheptane [HMS-5/7(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line. *g* = glassy, *k* = crystalline, *n* = nematic, *x* = unknown phase.

HMS-5/7(A/B)	M_n	M_w/M_n	Thermal transitions (°C), and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	17000	2.15	g 39 k 154 n 179(0.44) i g 31 k 123 n 143(0.04)* i	i 135(0.14) n 95(0.04) x 25 g
8/2	21200	2.05	g 33 k 146 n 168(0.63) i g 34 k 80 n 155(0.50) i	i 126(0.15) n 29 g
7/3	23000	2.44	g 30 k 142 n 184(0.59) i g 32 k 80 n 160(0.36) i	i 131(0.16) n 28 g
6/4	21100	2.25	g 28 k 135 n 185(0.60) i g 29 k 77 n 154(0.36) i	i 140(0.17) n 68(0.04) x 25 g
5/5	21600	2.24	g 27 k 113 n 192(0.52) i g 28 k 78 n 154(0.46) i	i 144(0.44) n 70(0.04) x 23 g
4/6	25800	1.81	g 27 k 115 n 184(0.59) i g 27 k 82 n 169(0.50) i	i 140(0.14) n 69(0.03) x 20 g
3/7	26800	2.65	g 24 k 122 n 177(0.60) i g 28 k 93 n 169(0.50) i	i 136(0.37) n 84(0.04) x 22 g
2/8	17200	2.38	g 30 k 130 n 178(0.51) i g 26 k 90 n 168(0.48) i	i 160(0.34) n 86(0.07) x 18 g
1/9	27200	2.68	g 30 k 137 n 178(0.61) i g 27 k 117 n 165(0.55) i	i 131(0.33) n 76(0.03) x 19 g
0/10	17200	2.56	g 29 k 145 n 178(0.55) i g 26 k 125 n 163(0.33) i	i 157(0.50) n 86(0.12) x 60 k 19 g

* Overlapped transitions.

annealing above the glass transition temperature this melting transition reappears. Annealing all samples at about 80°C for about five hrs provides a new heating scan which above 80°C displays melting endotherms which resemble those from the first heating scan. When the sample is annealed within the nematic phase for up to 8 hrs and rescanned, the isotropization transition temperature and its enthalpy change are about equal to those obtained from the first heating scan. Quantitative annealing experiments[7,56] demonstrate that the first heating scan corresponds to a quasi-equilibrium situation. That means, further annealing in the liquid crystalline phase during the first heating scan can still increase the isotropization temperature and its associated enthalpy change.

DSC cooling scans of HMS-9/11 are plotted in Figure 1b. HMS-11 and HMS-9/11 (1/9) display an isotropic-nematic transition followed by crystallization. All other HMS-9/11 copolymers and HMS-9 display an isotropic-nematic transition

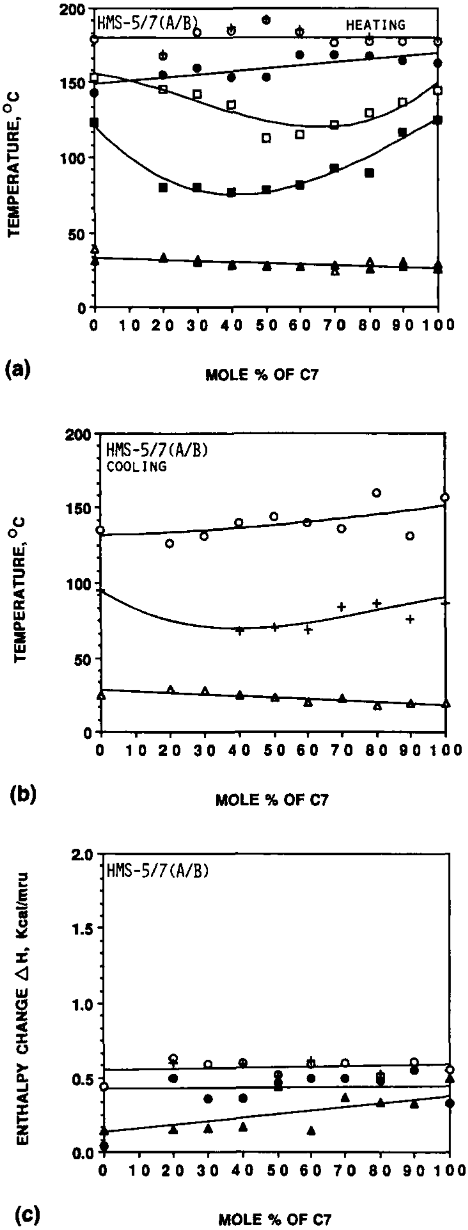


FIGURE 3 a) The dependence between thermal transition temperatures obtained from first and second heating scans and HMS-5/7(A/B) copolymer composition. T_g (Δ first scan, ▲ second scan), T_m (□ first scan, ■ second scan), T_{n-i} (○ first scan, ● second scan, + first scan after annealing at 80°C for 5 hrs). b) The dependence between thermal transition temperatures obtained from first cooling scan and HMS-5/7(A/B) copolymer composition. T_g (Δ), T_{n-s} (+), T_{i-n} (○). c) The dependence between the enthalpy change associated with the isotropization transition (ΔH_i) and HMS-5/7(A/B) copolymer composition. ○ first heating scan, ● second heating scan, ▲ cooling scan, + first heating scan after annealing at 80°C for 5 hrs.

TABLE III

Characterization of polyethers and copolyethers based on HMS, 1,9-dibromononane and 1,13-dibromotridecane [HMS-9/13(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line. *g* = glassy, *k* = crystalline, *n* = nematic, *x* = unknown phase.

HMS-9/13(A/B)	M_n	M_w/M_n	Thermal transitions (°C), and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	23500	2.75	g 26-k 135 n 169(0.53) i g 21 k 129 n 159(0.47) i	i 151(0.66) n 89 x 57 k 18 g
9/1	15100	2.16	k 126 n 161(0.70) i g 13 k 126 n 150(0.41) i	i 141(0.32) n 60 k 7 g
8/2	36600	2.68	g 24 k 117 n 160(0.80) i g 23 k 95 n 157(0.77) i	i 132(0.51) n 86(0.07) x 42 k 16 g
7/3	28000	2.40	g 14 k 102 n 153(0.69) i g 20 k 93 n 143(0.54) i	i 127(0.48) n 79(0.06) x 52 k 10 g
6/4	21000	2.86	g 24 k 101 n 160(0.69) i g 24 k 98 n 155(0.66) i	i 149(0.61) n 92(0.04) x 56 k 17 g
5/5	20800	2.63	g 20 k 100 n 146(0.72) i g 28 k 101 n 141(0.46) i	i 134(0.49) n 86(0.05) x 61 k 17 g
4/6	20700	2.70	g 20 k 106 n 151(0.70) i g 22 k 105 n 136(0.57) i	i 123(0.50) n 80(0.08) x 67 k 12 g
3/7	44000	2.53	g 35 k 120 n 153(0.87) i g 21 k 110 n 143(0.61) i	i 126(0.71) n 74 k 13 g
2/8	12900	1.93	g 18 k 105 n 143(0.73) i g 13 k 105 n 130(0.40) i	i 122(0.56) n 80 k 7 g
1/9	28200	2.50	g 37 k 125 n 149(0.51)* i g 22 k 123 n 143(0.34) i	i 121(0.63) n 89 k 16 g
0/10	24200	2.33	k 133 n 150(0.49)* i g 17 k 127 n 138 i	i 125(0.16)* n 99 k 9 g

* Overlapped transitions.

followed by a small nematic-smectic exotherm and a crystallization exotherm. The assignment of the nematic-smectic transition is not yet certain. X-ray diffraction experiments could not add additional evidence for or against it since the polymer crystallizes. Therefore, due to this uncertainty, over the entire manuscript we will label this phase transition as a nematic-x-phase transition. For the case of HMS-9/11(A/B) the *x*-phase is monotropic. This is due to the high degree of supercooling of the crystallization transitions (Figure 1b) versus the melting transitions (Figure 1a). As it will be discussed later, this crystallization process is strongly dependent on the spacer length.

All thermal transitions from Table I are plotted in Figures 2a, b, and c. Figure 2a plots glass transition, melting and isotropization temperatures as a function of

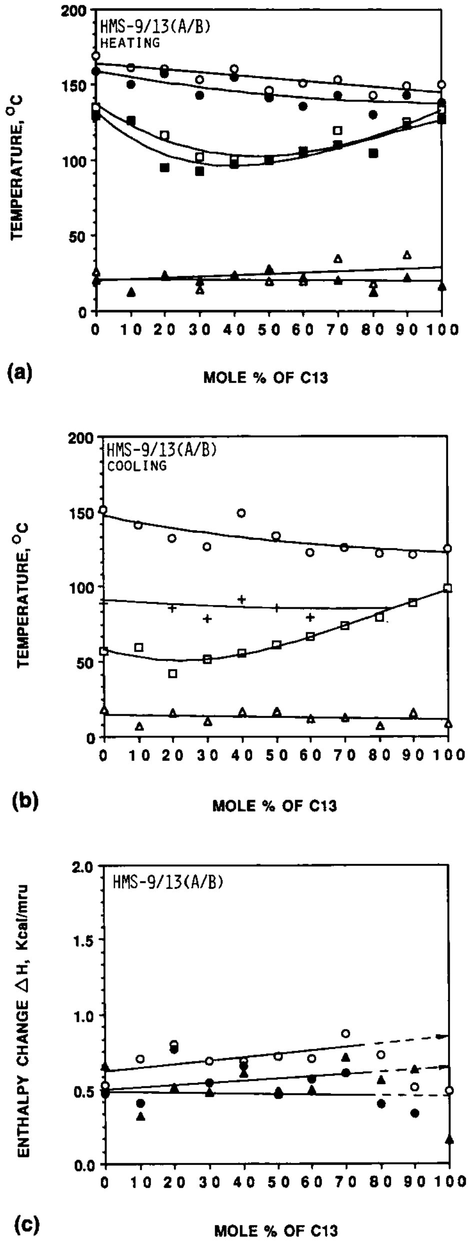


FIGURE 4 a) The dependence between thermal transition temperatures obtained from first and second heating scans and HMS-9/13(A/B) copolymer composition. T_g (Δ first scan, ▲ second scan), T_m (□ first scan, ■ second scan), T_{n-i} (○ first scan, ● second scan). b) The dependence between thermal transition temperatures obtained from first cooling scan and HMS-9/13(A/B) copolymer composition. T_g (Δ), T_{s-k} or T_{n-k} (□), T_{n-s} (+), T_{i-n} (○). c) The dependence between the enthalpy change associated with the isotropization transition (ΔH_i) and HMS-9/13(A/B) copolymer composition. ○ first heating scan, ● second heating scan, ▲ cooling scan.

TABLE IV

Characterization of polyethers and copolyethers based on HMS, 1,5-dibromopentane and 1,9-dibromononane [HMS-5/9(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line. *g* = glassy, *k* = crystalline, *n* = nematic, *x* = unknown phase.

HMS-5/9(A/B)	M_n	M_w/M_n	Thermal transitions (°C), and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	17000	2.15	g 39 k 154 n 179(0.44) i g 31 k 123 n 143(0.04)* i	i 135(0.14) n 95(0.04) x 25 g
8/2	15300	1.62	g 30 k 145 n 165(0.52) i g 32 k 66(0.03) n 138(0.10) i	i 127(0.24) n 26 g
7/3	30600	2.26	g 25 k 138 n 189(0.58) i g 27 k 77 n 166(0.33) i	i 143(0.25) n 75(0.01) x 20 g
6/4	19900	2.22	g 27 k 128 n 178(0.56) i g 27 k 80 n 158(0.48) i	i 137(0.43) n 73(0.05) x 21 g
5/5	16600	1.76	g 35 k 114 n 183(0.58) i g 20 k 80 n 158(0.32) i	i 131(0.35) n 76(0.04) x 14 g
4/6	14300	1.99	g 24 k 113 n 171(0.69) i g 28 k 161(0.57) i	i 135(0.46) n 81(0.10) x 14 g
3/7	11600	2.38	g 20 k 115 n 170(0.63) i g 19 k 148(0.39) i	i 123(0.30) n 75(0.02) x 11 g
2/8	36700	2.03	g 28 k 120 n 172(0.63) i g 24 k 90 n 156(0.40) i	i 143(0.51) n 81(0.09) x 16 g
1/9	28500	2.48	g 15 k 120 n 164(0.60) i g 23 k 107 n 150(0.40) i	i 140(0.38) n 79(0.02) x 16 g
0/10	23500	2.75	g 26 k 135 n 167(0.53) i g 21 k 129 n 159(0.47) i	i 151(0.66) n 89 x 51 k 18 g

* Overlapped transitions.

copolymer composition. Data obtained from both first and second heating scans are plotted in this figure. For the case of the isotropization temperature three sets of data are plotted: first and second heating scan and first heating scan after annealing in the nematic phase for five hours. The glass transition temperature data are identical regardless of the heating scan they were determined from, and show a linear dependence on copolymer composition. The melting temperatures of the homopolymers are strongly depressed upon copolymerization. The dependence between melting temperature and copolymer composition shows an eutectic at about 50/50 mole ratio between the two spacers. Data obtained from first heating scan are higher than those from second heating scans. Isotropization temperatures obtained from the second heating scan show a continuous dependence on copolymer composition. However, all these values are lower than those determined from the

TABLE V

Characterization of polyethers and copolyethers based on HMS, 1,5-dibromopentane and 1,11-dibromoundecane [HMS-5/11(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line. *g* = glassy, *k* = crystalline, *n* = nematic, *x* = unknown phase.

HMS-5/11(A/B)	M_n	M_w/M_n	Thermal transitions (°C), and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	17000	2.15	g 39-k 154 n 179(0.44) i g 31 k 123 n 143(0.04) i	i 135(0.14) n 95(0.04) x 25 g
9/1	20700	1.67	g 35 k 149 n 171(0.27) i g 33 k 134(0.15) i	i 128(0.13) n 30 g
8/2	24300	2.33	g 33 k 130 n 168(0.52) i g 26 k 85 n 155(0.34) i	i 140(0.12) n 76(0.04) x 20 g
7/3	31000	2.35	g 24 k 131 n 175(0.57) i g 25 k 79 n 150(0.30) i	i 141(0.33) n 19 g
6/4	19300	1.94	g 29 k 131 n 175(0.53) i g 26 k 83 n 151(0.49) i	i 132(0.14) n 72(0.01) x 19 g
5/5	22100	2.47	g 34 k 112 n 172(0.69) i g 28 k 90 n 157(0.28) i	i 127(0.26) n 74(0.05) x 21 g
4/6	25800	2.06	g 33 k 106 n 164(0.67) i g 26 k 94 n 155(0.62) i	i 126(0.33) n 84(0.05) x 35 k 19 g
3/7	18700	2.44	g 25 k 115 n 177(0.61) i g 21 k 112 n 152(0.50) i	i 145(0.61) n 61 k 13 g
2/8	23200	2.26	g 34 k 115 n 159(0.69) i g 27 k 111 n 145(0.40) i	i 123(0.37) n 78(0.02) x 50 k 17 g
1/9	25600	2.14	g 32 k 117 n 157(0.79) i g 23 k 111 n 147(0.40) i	i 138(0.50) n 62 x 49 k 12 g
0/10	18900	2.04	g 23 k 126 n 153(0.84) i g 15 k 122 n 143(0.35) i	i 124(0.44) n 94 k 9 g

first heating scan. Isotropization temperatures obtained from the first heating scan or after annealing are almost identical and show a linear dependence on copolymer composition.

Thermal transition temperatures determined from first cooling scan are plotted in Figure 2b. The crystallization temperature is strongly decreased and therefore, besides the enantiotropic nematic mesophase, a monotropic *x*-phase mesophase is observed. The dependence of the isotropic-nematic transition temperature versus copolymer composition resembles that of the nematic-isotropic transition temperature determined from the second heating scan (Figure 2d).

The isotropization enthalpy changes determined from the first heating scan and after annealing in the nematic mesophase, from the second heating scan and from the first cooling scan are plotted in Figure 2c. Data obtained from second heating

TABLE VI

Characterization of polyethers and copolyethers based on HMS, 1,7-dibromoheptane and 1,9-dibromononane [HMS-7/9(A/B)]. Data from the first heating and cooling scans are on the first line, and from the second heating scan on the second line. *g* = glassy, *k* = crystalline, *n* = nematic, *x* = unknown phase.

HMS-7/9(A/B)	M_n	M_w/M_n	Thermal transitions (°C), and corresponding enthalpy changes (kcal/mru) in parentheses	
A/B mol ratio	GPC		Heating	Cooling
10/0	17200	2.56	g 29 k 147 n 178(0.55) i g 26 k 125 n 163(0.33) i	i 157(0.50) n 86(0.12) x 60 k 19 g
9/1	16600	1.97	g 36 k 140 n 184(0.61) i g 21 k 120 n 165(0.60) i	i 135(0.45) n 83(0.04) x 62 k 14 g
8/2	16900	1.43	g 19 k 127 n 168(0.65) i g 16 k 109 n 160(0.64) i	i 132(0.40) n 82(0.04) x 11 g
7/3	31900	1.83	g 32 k 95 n 163(0.61) i g 28 k 80 n 156(0.59) i	i 127(0.31) n 76(0.04) x 20 g
6/4	30800	1.97	g 21 k 86 n 167(0.62) i g 20 k 92 n 160(0.49) i	i 132(0.47) n 84(0.07) x 13 g
5/5	12600	1.87	g 19 k 83 n 165(0.63) i g 19 k 92 n 137(0.20) i	i 128(0.21) n 73(0.03) x 15 g
4/6	31200	2.11	g 21 k 92 n 167(0.69) i g 26 k 94 n 155(0.62) i	i 123(0.19) n 65(0.04) x 17 g
3/7	16000	1.84	g 17 k 117 n 178(0.57) i g 21 k 90 n 149(0.28) i	i 136(0.17) n 80(0.02) x 27 k 12 g
2/8	30300	2.58	g 19 k 117 n 173(0.62) i g 19 k 96 n 158(0.52) i	i 151(0.48) n 84(0.06) x 16 g
1/9	17800	1.87	g 20 k 127 n 168(0.59) i g 22 k 127 n 157(0.51) i	i 150(0.43) n 86(0.05) x 41 k 11 g
0/10	23500	2.75	g 26 k 135 n 167(0.53) i g 21 k 129 n 159(0.47) i	i 151(0.66) n 89 x 51 k 18 g

and cooling scans are located on straight lines which have different slopes than the data collected from first heating scans or after annealing.

The most general conclusion resulting from this discussion is that the most meaningful data are those determined from the first heating scan. They correspond to a quasi-equilibrium situation. Better accuracy requires annealing and extrapolation to annealing time equal to infinity.[7,56]

Characterization of HMS-5/7 is summarized in Table II. From the number of melting endotherms only the one corresponding to crystalline-nematic transition is reported. Figure 3a presents the dependence between the glass transition, melting, and isotropization temperatures determined from first, second and for the isotropization temperature also after annealing, and copolymer composition. Thermal transitions determined from the cooling scans are plotted in Figure 3b, while the enthalpy changes associated with the isotropization transitions in Figure 3c. The plots from Figures 3a and 3c demonstrate that isotropization temperatures and their corresponding enthalpy changes determined from first heating scans are closer to equilibrium than data collected from second or subsequent heating scans or from any cooling scan.

Table III summarizes the characterization of the copolymer system HMS-9/13. Melting transitions presented in this table and in the following tables refer to crystalline-nematic transition only. Thermal transition temperatures from heating and cooling scans and the corresponding enthalpy changes of isotropization are plotted in Figures 4a, b, and c. The phase behavior of this system resembles that of HMS-9/11. The main difference consists in the fact that the melting and nematic-isotropic transition temperatures are overlapped for both HMS-13 and for HMS-9/13 (1/9) and therefore the corresponding enthalpy changes could not be calculated directly from the DSC scans (Table III). They were, however, determined by the extrapolation of the plot of the enthalpy changes of isotropization vs composition to HMS-9/13 (1/9) and HMS-13, respectively.

The characterization results on HMS-5/9, HMS-5/11 and HMS-7/9 are summarized in Tables IV, V and VI, respectively. The phase behavior of all these systems resembles that of HMS-5/7 which was presented in Figure 3.

Table VI presents the thermal behavior determined from the first and second heating scans and from the first cooling scans obtained from DSC experiments performed at 10°C/min and 20°C/min, for several copolymers. Phase transition temperatures determined from the first heating scan are very little dependent on the DSC heating rate. The isotropization transition temperature determined from second heating scans is consistently higher when it is determined with a lower heating rate. Exception is the system HMS-9/13 (4/6) where this data might have been subjected to a higher experimental error. This trend represents additional evidence for a kinetically controlled isotropization temperature and for the quasi-equilibrium nature of the isotropization temperatures as determined from first heating scans.

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