Polymerization of 5-9

Polymerizations were carried out in sealed tubes at 60 °C in bulk or benzene using AIBN (3 mol %) and at 120 °C in bulk or in chlorobenzene using di-*tert*-butyl peroxide (DTBP) (3 mol %) as an initiator. The polymers obtained at 60 °C in bulk and benzene were purified by dissolution in hot DMSO (80 °C; the polymers from **5**, **6**, **8**) or *m*-cresol (the polymers from **7**), followed by precipitation in ether (the polymers from **5**, **6**, **8**) or a mixture of ether and triethylamine (9/1) (the polymers from **7**). The polymers obtained at 120 °C were purified by dissolution in hot DMSO (130 °C, the polymers from **5**, **6** in bulk and chlorobenzene, **8** in bulk; 120 °C, the polymers from **9**) or in *m*-cresol (the polymers from **7** in bulk and chlorobenzene, **8** in chlorobenzene), followed by precipitation in ether (the polymers from **5**, **6** in bulk and chlorobenzene, **8** in bulk, **9**) or a mixture of ether and triethylamine (9/1) (the polymers from **7** in bulk and chlorobenzene, **8** in chlorobenzene). The precipitated polymers were separated by filtration, thoroughly washed with ether, and dried under reduced pressure at room temperature.

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Registry No. 1, 123640-21-1; **2**, 86184-69-2; **3**, 22195-38-6; **4**, 86184-54-5; **5**, 123640-22-2; **5** (homopolymer), 123640-33-5; **6**, 123640-23-3; **6** (homopolymer), 123640-34-6; **7**, 108121-82-0; **7** (homopolymer), 108121-83-1; **8**, 123640-24-4; **8** (homopolymer), 123640-35-7; **9**, 123640-25-5; **9** (homopolymer), 123640-36-8; **12**, 96-24-2; AIBN, 78-67-1; benzoyl peroxide, 94-36-0; 4,4'-dimethoxybenzophenone, 90-96-0; 4,4'-dimethylbenzophenone, 611-97-2; 4,4'-dichlorobenzophenone, 90-98-2.

References and Notes

(1) Hiraguri, Y.; Endo, T. *J. Am. Chem. Soc.* **1987**, *109*, 3779.

(2) (a) Walling, C.; Briggs, E. R.; Wolfstrin, K. B.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 1537. (b) Imoto, M.; Kinoshita, M.; Nishigaki, M. *Makromol. Chem.* **1965**, *86*, 217. (c) Kinoshita, M.; Imoto, M. *Kogyo Kagaku* Zasshi **1965**, *68*, 2454. (d) Imoto, M.; Takemoto, K. *Nippon Kagaku Kaishi* **1975**, 177; *Chem. Abstr.* **1975**, *82*, 98529u. (e) Giese, B.; Meister, J. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 178.

(3) (a) Imoto, M.; Ouchi, T. *Nippon Kagaku Kaishi* **1986**, 585; *Chem. Abstr.* **1986**, *104*, 225278n. (b) Imoto, M.; Ouchi, T. *Nippon Kagaku Kaishi* **1987**, 894; *Chem. Abstr.* **1987**, *107*, 23785b.

(4) (a) Henri, R. O.; Texier, F. *J. Chem. Educ.* **1978**, *55*, 437. (b) Imoto, M.; Nagaya, T. In *Yuukihannouron*; Tokyo Kagaku Dojin: Tokyo, 1982; p 411.

(5) Klemm, L. H.; Bower, G. W. *J. Org. Chem.* **1957**, *23*, 344.

(6) Noguchi, A.; Igawa, T.; Shimada, Y. *Yuki Gosei Kagaku Kyokaishi* **1963**, *21*, 377; *Chem. Abstr.* **1963**, *59*, 5060f.

(7) Hiraguri, Y.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* in press.

(8) Humphreys, R. W. R.; Arnold, D. R. *Can. J. Chem.* **1977**, *55*, 2286.

Liquid Crystalline Polyethers Based on Conformational Isomerism. 6.[†] Influence of Copolymer Composition of a Ternary Copolyether Based on 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane, 1,5-Dibromopentane, 1,7-Dibromoheptane, and 1,9-Dibromononane on Its Mesomorphic Phase Transitions

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ABSTRACT: Ternary copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE), 1,5-dibromopentane, 1,7-dibromoheptane, and 1,9-dibromononane [MBPE-5/7/9(*A*/*B*/*C*)] were synthesized, and their mesomorphic phase behavior was characterized by differential scanning calorimetry and optical polarized microscopy. Three-dimensional representations of experimental data demonstrated that isomorphic–mesomorphic phase transition temperatures and enthalpy changes of all copolymers are situated on planar surfaces that represent the weight-averaged values of the corresponding thermal transitions and enthalpy changes of the MBPE-5, MBPE-7, and MBPE-9 homopolymers.

Introduction

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

The most reliable and simple synthetic technique that is used to manipulate the structure of polymers, and the least understood in the field of liquid crystalline polymers is copolymerization.[1-4] Main-chain liquid crystalline polymers and copolymers are synthesized by step polymerizations that are based on reversible or irreversible reactions. In contrast to chain copolymerizations, step copolymerizations performed in a homogenous phase

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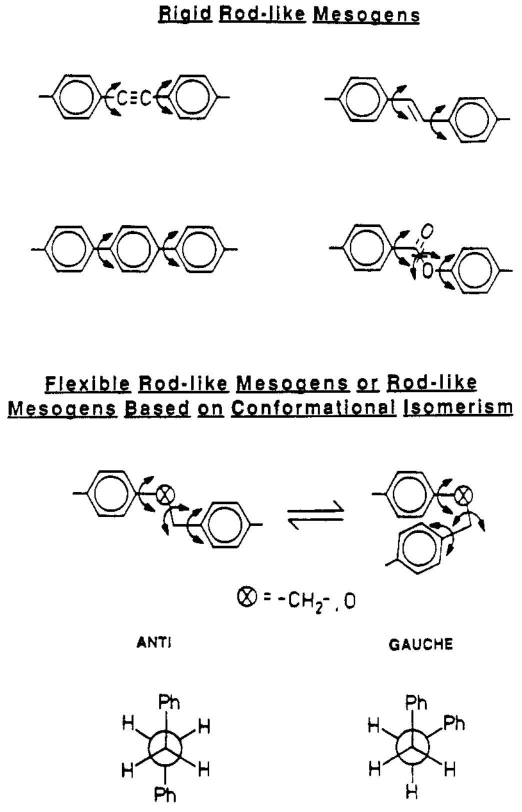
at high conversion and with a stoichiometric ratio between comonomers always lead to copolymer compositions that are identical with the comonomers feed. This implies that the compositional heterogeneity of the copolymers obtained by step reactions is lower than that of copolymers synthesized by chain 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, sequence distribution is thermodynamically controlled and the copolymer microstructure is determined by redistribution reactions. The thermodynamic driving force toward a certain copolymer microstructure is provided by the nature of the phase in which copolymerization is performed. The copolymer sequence distribution[5-7] and the configuration of the structural units[8,9] 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 on the basis of the "bootstrap model", and its implications were recently reviewed.[10] Some of the most recent examples of "bootstrap effects" were observed in the radical copolymerization of macromonomers,[11] in the synthesis of block copolymers from immiscible amorphous segments,[12,13] and in the synthesis of ternary copolymers from monomers that can give rise to amorphous and liquid crystalline structural units by reversible copolymerization reactions.[14]

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 sequence distribution 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 the kinetic point of view,[15] they are treated as one-phase solution polymerizations.

In the previous papers[16-20] from this series we have advanced the concept of flexible rodlike mesogenic units or rodlike mesogenic units based on conformational isomerism (Chart I). This concept was used in the synthesis of both quasi-rigid liquid crystalline polyethers[16] (i.e., polyetherswithout flexible spacers) and semiflexible polyethers and copolyethers based on flexible mesogenic units and flexible spacers.[17-20] 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) is a suitable mesogenic unit for copolymerization studies since its homopolyethers and copolyethers containing flexible spacers based on an even number or an odd number of methylene units provide high molecular weight polymers that are soluble in conventional organic solvents.[17-20]

Three categories of copolymerization experiments were performed so far: copolymerizations based on MBPE and pairs of two flexible spacers containing odd numbers of methylene units,[17,18] even numbers of methylene units,[19] and combinations of odd and even numbers of methylene units.[20] The same conclusion was obtained from all three series of experiments. Copolymerization depresses the rate of crystallization and, subsequently, transforms virtual or monotropic mesophases into enantiotropic mesophases. However, identical mesophases of copolymers display both thermal transition temperatures and enthalpy changes that represent weight-averaged values of the corresponding parameters of parent homopolymers.[17-20] This conclusion agrees with similar experimental data reported from several other laboratories.[21-25] It demonstrates that copolymerization not only does represent one of the most powerful techniques available to manipulate polymer-phase transitions but also becomes the only available synthetic tool that can be used to determine virtual mesomorphic phase transitions and thermodynamic parameters of homopolymers.

Chart I



A complete elucidation of our ability to tailor-make mesomorphic phase transitions in flexible liquid crystalline polymers by copolymerization requires some additional experiments. One of them will represent the subject of this paper and refers to ternary copolymers based on a single mesogenic unit and three different flexible spacers. The particular example described here refers to copolyethers based on MBPE and 1,5-dibromopentane, 1,7-dibromoheptane, and 1,9-dibromononane.

Experimental Section

Materials. 1,5-Dibromopentane (97%), 1,7-dibromoheptane (97%), 1,9-dibromononane (97%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), and *o*-dichlorobenzene (99%) (all from Aldrich) were used as received. 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) was synthesized as previously reported.[17] Its purity was higher than 99.9% (HPLC); mp (DSC, 20 °C/min) 148 °C.

Synthesis of Copolyethers. The synthesis of polyethers and copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-dibromoalkanes is outlined in Scheme II. Conventional liquid–liquid two-phase (organic solvent–aqueous NaOH solution) phase-transfer-catalyzed polyetherification conditions were used for the preparation of the polyethers and copolyethers.[17,26,27] Polyetherifications were carried out under nitrogen atmosphere at 80 °C in o-dichlorobenzene–10 N NaOH–water solution (10 times the molar excess of NaOH versus phenol groups) in the presence of TBAH (10 mol % of phenol groups) as phase-transfer catalyst. The ratio of nucleophilic monomers to electrophylic monomers was in every case 1.0/1.0. The reaction mixture was stirred at 1000 rpm with a magnetic stirrer for 6 h. Afterwards, the organic and aqueous layers were diluted with chloroform and water, respectively, and the aqueous layer was removed. The organic layer was washed several times with water, followed by dilute hydrochloric acid and finally with water again. The polymer was separated by precipitation of the polymer solution into methanol to obtain a white fibrous precipitate. Yields were higher than 90% in most cases. All polymers were further purified by two successive precipitations from chloroform solutions; first into acetone and then into methanol.

Over the entire paper the polyethers will be designated MBPE-X where X is the number of methylene units in the spacer. Similarly, binary copolyethers will be designated MBPE-$X/Y(A/B)$ 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. Ternary copolymers will be designated MBPE-5/7/9($A/B/C$) where $A/B/C$ refers to the molar ratio of the three 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 10LC equipped with an LC 100 column oven, LC 600 autosampler, and a Sigma 15 data station. The measurements were made by using the UV detector, tetrahydrofuran 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 Å, 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 unless stated. 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 the heat capacity. All heating and cooling scans after the first heating scan produced perfectly reproducible data. The transitions reported in Table I were taken from the second or third heating or cooling scans. As discussed in detail elsewhere,[18] different thermal histories are strongly influencing the thermal behavior of these polymers.

A Carl Zeiss optical polarizing microscope (magnification 100×) equipped with a Mettler FP82 hot stage and a Mettler 800 central processor was used to observe the thermal transitions and to analyze the textures.[28,29]

Analysis of Experimental Data. Mesomorphic thermal transition temperatures, their corresponding enthalpy changes, and the glass transition temperatures determined from heating and cooling scans (Table I) were fitted according to a linear regression to the following equation

$$T \text{ or } \Delta H = aA + bB + cC$$

where $A + B + C = 100$.[30] a, b, and c are constants, and A, B, and C represent the molar concentrations of the flexible spacers containing 5, 7, and 9 methylene units, respectively. A computer software[31] was used to determine the parameters a, b, and c and the multiple linear correction coefficients (MLCC) which are reported in Table II. The calculation of copolymer phase transition temperatures and enthalpy changes reported in Table I was done by using the same equation (T or $\Delta H = aA + bB + cC$) and the parameters a, b, and c from Table II.

Results and Discussion

Representative second heating and cooling DSC scans of MBPE-5, MBPE-7, MBPE-9, and MBPE-5/7/9(33/33/33) are presented in parts a and b of Figure 1, respectively. As determined from second heating and cooling DSC scans obtained with 20 °C/min, MBPE-7 is crystalline, while both MBPE-5 and MBPE-9 exhibit monotropic nematic and smectic mesophases. MBPE-5 crystallizes on the heating scan only and displays two crystalline melting transitions at 79 and 115 °C. The ratio between the enthalpy changes associated with these two meltings is strongly dependent on the thermal history of the sample. MBPE-9 crystallizes on the cooling scan. Upon copolymerization of two or more than two flexible spacers with MBPE, the rate of crystallization of the resulting copolymers is drastically suppressed, and the monotropic or virtual liquid crystalline mesophases become enantiotropic for most copolymer compositions. MBPE-5/7/9(33/33/33) represents a typical example. The second heating and cooling DSC scans of this copolymer display both nematic and smectic enantiotropic mesophases and no crystallization (Figure 1a,b).

Binary copolymers based on multiple combinations of MBPE-5, MBPE-7, MBPE-9, and MBPE-11 were synthesized and characterized both by dynamic DSC measurements[17] and under quasi-equilibrium conditions.[18] Liquid crystalline thermal transitions and the corresponding enthalpy changes of isomorphic or identical mesophases of these copolymers display linear dependences of copolymer composition. The extrapolation of these plots led to the determination of the virtual liquid crystalline transitions and enthalpy changes of the parent homopolymers. The average phase transition temperatures and enthalpy changes of MBPE-5, MBPE-7, and MBPE-9 as determined from multiple sets of binary copolymers are summarized in Table III.[17] They demonstrate that all three homopolymers present nematic and smectic mesophases that are either virtual or monotropic.

It is essential that number-average molecular weights of all polymers under consideration be higher than 12 000. Below this value, mesomorphic phase transitions are still molecular weight dependent.[26,27] A brief inspection of Table I shows that all molecular weights of the polymers are well above this limit. An additional comment has to be made at this point. If we inspect Scheme I, we observe that MBPE units inserted within the structure of polyethers and copolyethers give rise to constitutional isomeric structural units which according to the reactivity of the two phenol groups of MBPE should lead to a statistical distribution. Therefore, if we consider the constitutional isomeric structural units derived from MBPE, terpolymer does not represent the proper name for our copolymers since they contain more than three structural units. Nevertheless, we will continue to consider these copolymers as being terpolymers based on the number of different monomeric units that differ only through their chemical composition.

Table I summarizes copolymer compositions, molecular weights, experimental and calculated phase transition temperatures, and thermodynamic parameters for MBPE-5/7/9($A/B/C$) systems. Experimental data for MBPE-5/7, MBPE-5/9, and MBPE-7/9 copolymers were obtained from a previous publication.[17]

Let us first discuss the experimental results collected from the cooling DSC scans.

Figure 2a presents the plot of the experimental isotropic–nematic transition temperatures (T_{in}) as a function of

Table I

Characterization of Copolyethers Based on MBPE and 1,5-Dibromopentane, 1,7-Dibromoheptane, and 1,9-Dibromononane (MBPE-5/7/9(*A*/*B*/*C*)): Experimental Data (on First Line) on Each Copolymer and Data Calculated Based on the Multiple Linear Regression of the Experimental Data (on Second Line)

MBPE-5/7/9(*A*/*B*/*C*)	GPC		thermal transitns (°C) and corresponding enthalpy changes (kcal/mol)	
A/*B*/*C* ratio	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	heating	cooling
33/33/33	18 300	1.38	g 11 s 59 (0.16) n 70 (0.75) i	i 63 (0.72) n 54 (0.16) s 6 g
			g 11 s 57 (0.14) n 69 (0.71) i	i 61 (0.73) n 51 (0.14) s 5 g
30/40/30	32 000	2.24	g 9 s 55 (0.13) n 68 (0.67) i	i 62 (0.68) n 52 (0.11) s 6 g
			g 11 s 58 (0.14) n 70 (0.72) i	i 62 (0.74) n 52 (0.14) s 5 g
30/30/40	21 300	1.82	g 9 s 58 (0.15) n 70 (0.75) i	i 63 (0.73) n 53 (0.12) s 3 g
			g 11 s 59 (0.14) n 71 (0.74) i	i 63 (0.76) n 52 (0.13) s 4 g
40/30/30	20 400	1.88	g 9 s 52 (0.14) n 65 (0.60) i	i 59 (0.61) n 48 (0.14) s 3 g
			g 12 s 56 (0.14) n 69 (0.69) i	i 61 (0.71) n 50 (0.14) s 5 g
20/60/20	20 000	1.84	g 10 s 59 (0.15) n 71 (0.77) i	i 64 (0.75) n 53 (0.13) s 4 g
			g 11 s 59 (0.15) n 71 (0.74) i	i 63 (0.75) n 53 (0.15) s 4 g
20/40/40	18 600	1.42	g 9 s 60 (0.15) n 71 (0.82) i	i 65 (0.79) n 55 (0.15) s 3 g
			g 10 s 60 (0.14) n 72 (0.77) i	i 64 (0.79) n 54 (0.14) s 4 g
20/20/60	23 200	1.75	g 9 s 62 (0.13) n 73 (0.81) i	i 66 (0.84) n 57 (0.14) s 4 g
			g 9 s 61 (0.14) n 73 (0.80) i	i 65 (0.83) n 55 (0.13) s 3 g
40/20/40	17 000	1.36	g 8 s 54 (0.18) n 66 (0.73) i	i 61 (0.72) n 50 (0.16) s 3 g
			g 12 s 57 (0.14) n 69 (0.70) i	i 61 (0.73) n 50 (0.13) s 5 g
60/20/20	31 100	2.24	g 16 s 52 (0.10) n 65 (0.58) i	i 56 (0.60) n 45 (0.11) s 9 g
			g 14 s 53 (0.14) n 65 (0.60) i	i 57 (0.63) n 46 (0.13) s 7 g
40/40/20	17 700	2.44	g 13 s 51 (0.13) n 64 (0.58) i	i 57 (0.58) n 45 (0.12) s 6 g
			g 12 s 56 (0.14) n 68 (0.67) i	i 60 (0.69) n 49 (0.14) s 6 g
10/80/10	28 500	1.82	g 12 k 77 (1.60) i	i 66 (0.77) n 55 (0.14) s 7 g
			g 11 s [60 (0.15)] n [72 (0.76)]	i 65 (0.77) n 54 (0.16) s 4 g
10/60/30	27 700	1.82	g 11 s 60 (0.12) n 72 (0.72) i	i 64 (0.76) n 53 (0.13) s 4 g
			g 10 s 61 (0.15 n 73 (0.79) i	i 65 (0.81) n 55 (0.15) s 3 g
10/30/60	26 900	1.97	g 10 s 64 (0.13) n 75 (0.91) i	i 68 (0.90) n 59 (0.15) s 4 g
			g 8 s 63 (0.14) n 74 (0.83) i	i 67 (0.86) n 57 (0.13) s 2 g
10/10/80	28 900	2.02	g 10 k 60 (0.07) k 80 (1.24) i	i 69 (0.96) n 60 (0.13) s 4 g
			g 8 s [64 (0.13)] n [75 (0.86)] i	i 68 (0.90) n 58 (0.12) s 2 g
30/10/60	30 400	2.54	g 10 s 59 (0.11) n 71 (0.76) i	i 64 (0.77) n 54 (0.12) s 5 g
			g 10 s 60 (0.13) n 71 (0.77) i	i 63 (0.80) n 53 (0.12) s 4 g
60/10/30	27 000	2.32	g 13 s 52 (0.10) n 64 (0.57) i	i 58 (0.60) n 46 (0.11) s 8 g
			g 14 s 53 (0.13) n 66 (0.62) i	i 57 (0.65) n 46 (0.13) s 7 g
80/10/10	24 800	2.12	g 18 s 48 (0.10) n 61 (0.52) i	i 52 (0.49) n 39 (0.07) s 10 g
			g 16 s 49 (0.13) n 62 (0.52) i	i 53 (0.54) n 41 (0.13) s 9 g
60/30/10	17 200	1.28	g 13 s 51 (0.16) n 63 (0.65) i	i 57 (0.63) n 46 (0.17) s 7 g
			g 14 s 52 (0.14) n 65 (0.59) i	i 56 (0.61) n 45 (0.14) s 8 g
30/60/10	26 300	1.62	g 13 s 59 (0.15) n 71 (0.75) i	i 64 (0.73) n 54 (0.14) s 7 g
			g 12 s 57 (0.15) n 69 (0.69) i	i 61 (0.70) n 51 (0.15) s 5 g
100/0/0	19 000	1.90	g 20 k 79 (1.44) k 115 (0.33) i	i 51 (0.57) n 37 (0.10) s 13 g
			g 18 s [45 (0.13)] n [58 (0.44) i	i 50 (0.46) n 37 (0.13) s 11 g
80/20/0	21 700	1.77	g 19 s 51 (0.15) n 65 (0.58) i	i 55 (0.61) n 43 (0.16) s 12 g
			g 16 s 48 (0.14) n 61 (0.51) i	i 53 (0.52) n 41 (0.13) s 9 g
60/40/0	22 500	1.73	g 14 s 51 (0.15) n 64 (0.57) i	i 54 (0.60) n 43 (0.16) s 7 g
			g 15 s 51 (0.14) n 64 (0.57) i	i 56 (0.59) n 45 (0.14) s 8 g
50/50/50	20 700	1.85	g 14 s 55 (0.16) n 68 (0.62) i	i 58 (0.65) n 48 (0.17) s 7 g
			g 14 s 53 (0.14) n 66 (0.61) i	i 58 (0.62) n 46 (0.15) s 7 g
40/60/0	25 300	1.73	g 14 s 58 (0.13) n 70 (0.62) i	i 59 (0.64) n 48 (0.17) s 6 g
			g 13 s 55 (0.15) n 67 (0.64) i	i 59 (0.65) n 48 (0.15) s 6 g
20/80/0	24 800	1.96	g 13 k 63 (0.11) n 77 (1.55) i	i 62 (0.71) n 51 (0.15) s 5 g
			g 12 s [58 (0.15)] n [70(0.71)] i	i 62 (0.72) n 52 (0.16) s 5 g
0/100/0	22 100	1.76	g 7 k 85 (2.18) i	i 66 (2.01) k 0 g
			g 10 s [61 (0.16)] n [73(0.78)] i	i [66 (0.78)] n [56 (0.17)] s 4 g
0/80/20	29 100	2.04	g 11 k 62 (0.21) k 79 (1.91) i	i 67 (0.85) n 58 (0.14) s 38 (0.09) k 3 g
			g 9 s [62 (0.15)] n [74 (0.81)] i	i 67 (0.82) n 57 (0.16) s 3 g
0/60/40	26 600	1.94	g 8 s 63 (0.14) n 75 (0.80) i	i 67 (0.84) n 57 (0.17) s 3 g
			g 9 s 63 (0.15) n 75 (0.84) i	i 67 (0.86) n 58 (0.15) s 2 g
0/50/50	29 100	1.87	g 9 s 66 (0.15) n 78 (0.89) i	i 68 (0.91) n 59 (0.15) s 2 g
			g 8 s 64 (0.14) n 75 (0.,5) i	i 68 (0.88) n 58 (0.14) s 2 g
0/40/60	23 000	1.64	g 8 s 65 (0.14) n 77 (0.89) i	i 68 (0.91) n 59 (0.16) s 2 g
			g 8 s 64 (0.14) n 76 (0.87) i	i 68 (0.89) n 59 (0.14) s 2 g
0/20/80	27 000	1.84	g 9 k 50 (0.23) k 67 (0.06) k 82 (1.91) i	i 70 (0.98) n 60 (0.14) s 2 g
			g 7 s [66 (0.14)] n [77 (0.90)] i	i 69 (0.93) n 60 (0.13) s 1 g
0/0/100	20 600	1.38	g 6 k 75 k 80 k 91 (4.02) i	i 69 (1.05) n 58 (0.06) s 48 (2.13) k 0 g
			g 6 s [67 (0.13)] n [77 (0.93)] i	i 70 (0.97) n 61 (0.12) s 0 g
80/0/20	24 300	1.80	g 15 s 51 (0.13) n 64 (0.54) i	i 53 (0.58) n 42 (0.15) s 7 g
			g 15 s 49 (0.13) n 62 (0.54) i	i 54 (0.56) n 42 (0.12) s 9 g
60/0/40	20 100	1.63	g 11 s 54 (0.15) n 64 (0.62) i	i 57 (0.65) n 47 (0.17) s 4 g
			g 13 s 54 (0.13) n 66 (0.63) i	i 58 (0.66) n 47 (0.12) s 7 g
50/0/50	18 000	1.66	g 9 s 56 (0.14) n 68 (0.67) i	i 60 (0.72) n 49 (0.17) s 2 g
			g 12 s 56 (0.13) n 68 (0.68) i	i 60 (0.72) n 49 (0.12) s 5 g
40/0/60	30 200	1.76	g 11 s 62 (0.13) n 74 (0.71) i	i 62 (0.69) n 53 (0.10) s 2 g
			g 11 s 58 (0.13) n 70 (0.73) i	i 62 (0.77) n 51 (0.12) s 4 g
20/0/80	26 700	2.01	g 9 k 62 k 74 n 80 (1.17)[a] i	i 64 (0.81) n 54 (0.11) s 1 g
			g 8 s [62 (0.13)] n [74 (0.83)] i	i 66 (0.87) n 56 (0.12) s 2 g

[a] Overlapped transitions; virtual transitions in brackets.

Table II
Parameters Obtained from the Linear Regression of the Experimental Data from Table I According to the Equation T or $\Delta H = aA + bB + cC$

parameter	a	b	c	MLCC[a]	deg of freedom
$T_{g(h)}$[b]	0.18	0.10	0.06	0.86	34
T_{sn}	0.45	0.61	0.67	0.91	25
ΔH_{sn}	0.0013	0.0016	0.0013	0.27	25
T_{ni}	0.58	0.73	0.77	0.89	25
ΔH_{ni}	0.0044	0.0078	0.0093	0.91	25
T_{in}	0.49	0.66	0.70	0.97	33
ΔH_{in}	0.0046	0.0078	0.0097	0.93	33
T_{ns}	0.37	0.56	0.61	0.96	33
ΔH_{ns}	0.0012	0.0017	0.0012	0.38	33
$T_{g(c)}$[b]	0.11	0.036	0.0014	0.84	34

[a] MLCC = multiple linear correction coefficient. [b] $T_{g(h)} = T_g$ from heating scan; $T_{g(c)} = T_g$ from cooling scan.

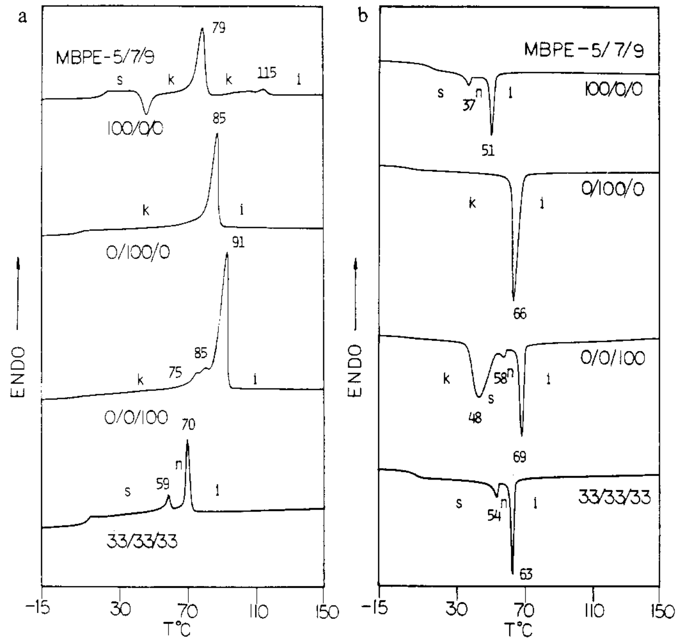


Figure 1. Heating (a) and cooling (b) DSC thermograms (20 °C/min) of MBPE-5, MBPE-7, MBPE-9, and MBPE-5/7/9(33/33/33).

copolymer composition. All experimental thermal transition temperatures are located on a plane surface. However, the shaded plane surface from Figure 2a corresponds to the surface associated with the calculated T_{in} values from Table I. There is very good agreement between the experimental and calculated T_{in} data from Table I and between the calculated and experimental plane surfaces from Figure 2a. This agreement is confirmed by the excellent value of the multiple linear correction coefficient for T_{in} from Table II. The calculated plane surface from Figure 2a was extrapolated by computer and led to the determination of the T_{in} values for MBPE-5, MBPE-7, and MBPE-9, which are available in Table III. Again we observe perfect agreement between the real and virtual T_{in} values determined either experimentally or calculated from binary or ternary copolymers.

Figure 2b presents the plot of the experimental nematic–smectic transition temperatures (T_{ns}) as a function of copolymer composition. The shaded plane surface, which was built with calculated T_{ns} values, overlaps the experimental T_{ns} data. The agreement between calculated and experimental T_{ns} data is again very good (Table I). This statement is supported by the very good value of the multiple linear correction coefficient corresponding to T_{ns} ratio (Table II). The extrapolation of the calculated plane surface from Figure 2b led to the determination of the T_{ns} data for homopolymers (Table III). There is very good agreement between the T_{ns} data for homopolymers calculated from binary and ternary copolymers.

Finally, Figure 2c plots the experimental enthalpy changes associated with both the isotropic–nematic (ΔH_{in}) and nematic–smectic (ΔH_{ns}) transition temperatures. The shaded plane surfaces are obtained with calculated data and agree very well with the experimental points. The multiple linear correction coefficient for ΔH_{in} is very good. However, there is a larger discrepancy between the calculated and experimental data of ΔH_{ns} (MLCC = 0.3841) (Table II). This can be easily explained on the basis of the very low intrinsic values of ΔH_{ns} (Table I). The ΔH_{ns} values extrapolated from the binary and ternary copolymerization experiments are reported in Table III and show very good agreement.

The experimental data obtained from the heating DSC scans of MBPE-5/7/9(*A*/*B*/*C*) copolymers are plotted in Figure 3a–c. The shaded plane surfaces correspond to calculated values of the nematic–isotropic and smectic–nematic thermal transition temperatures (T_{ni} and T_{sn}) and of the corresponding enthalpy changes (ΔH_{ni} and ΔH_{sn}). The agreement between experimental and calculated data is very good. The extrapolated of these three plane surfaces led to the determination of the virtual T_{ni}, T_{sn}, ΔH_{ni}, and ΔH_{sn} for MBPE-5, MBPE-7, and MBPE-9. These data are summarized in Table III together with the corresponding data obtained from binary copolymers. They agree again very well. The least accuracy is obtained for the case of ΔH_{sn} (MLCC = 0.2739) (Table II). This is due to the very low values of the enthalpy changes associated with the T_{sn} (Table I).

All MBPE-5/7/9(*A*/*B*/*C*) copolymers exhibit textures that are similar to those of the textures displayed by the previously described binary copolymers.[17] The copolymers that display only liquid crystalline transitions on their DSC cooling scans (Table I) can be maintained as anisotropic glasses below their glass transition temperature. However, as demonstrated previously for the case of binary copolymers,[18] annealing at proper temperatures located above their glass transition temperature and for suitable thermal histories induces their crystallization. The rate of crystallization of the ternary copolymers is however lower than the rate of crystallization of binary copolymers. This behavior supports our previous statement[17-20] that transformation of a monotropic or virtual mesophase into an enantiotropic mesophase by copolymerization represents a kinetic effect.

We believe the results of this experiment are very important since they definitively demonstrate that transition temperatures and the corresponding thermodynamic parameters of isomorphic or identical mesophases of statistical binary,[17-20] of ternary, and of any other multicomponent main-chain copolymers based on chemically similar structural units represent weight-averaged values of those of the parent homopolymers. Therefore, they behave as ideal phase diagrams of isomorphic low molar liquid crystals. On the basis of these results, we can assume that the dependence between phase transitions temperatures and the thermodynamic parameters of copolymers and copolymer composition of main-chain liquid crystalline copolymers resemble the rules of miscibility derived by Arnold, Sackmann, and Demus for low molar mass liquid crystals.[32-34] This can be translated to the field of liquid crystalline polymers and copolymers in the following way: if the liquid crystalline phases exhibited by two homopolymers are fully miscible, they are isomor-

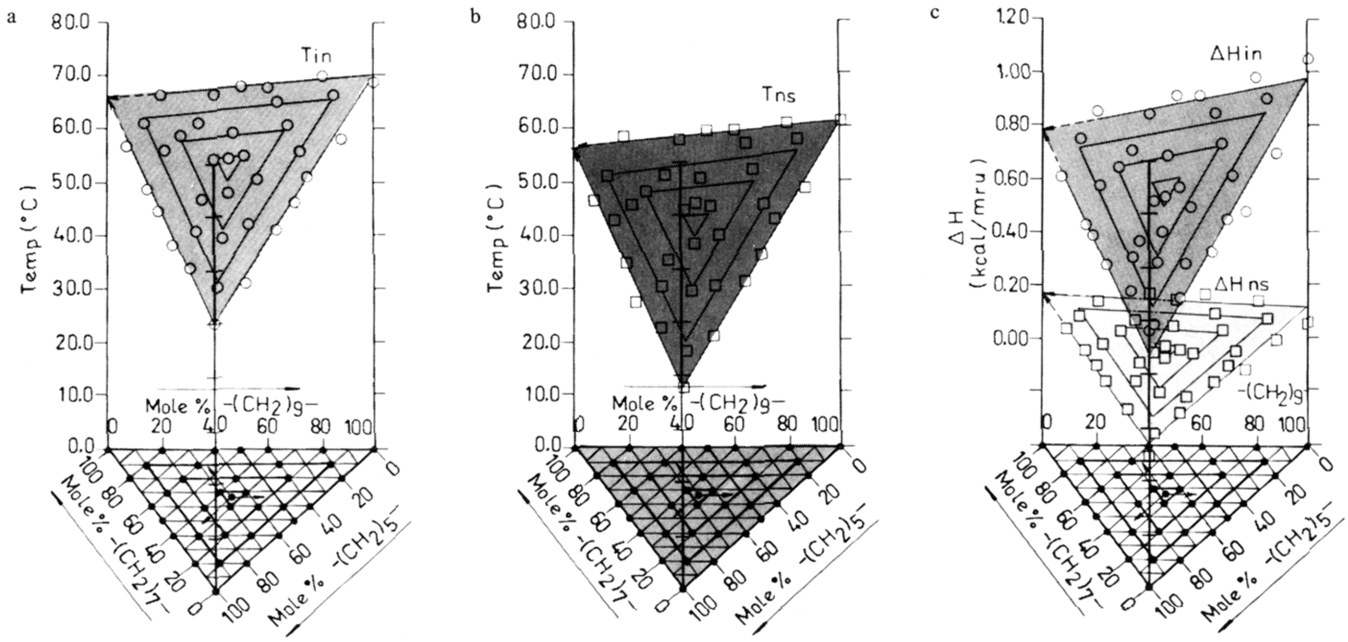
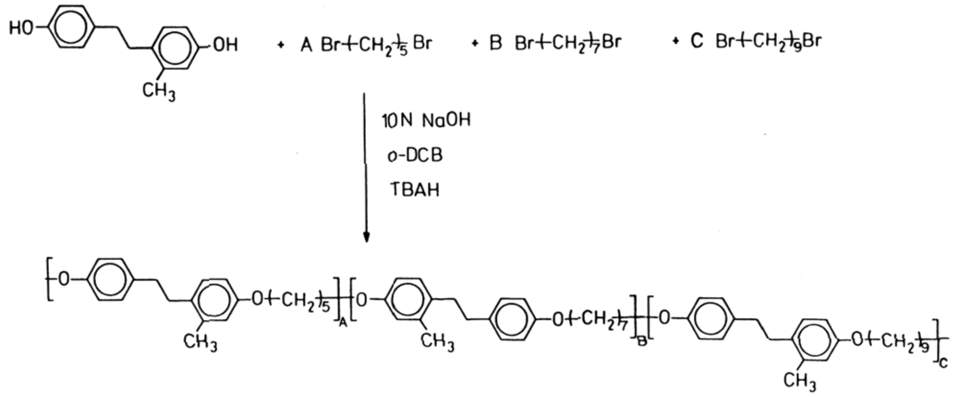


Figure 2. (a) Experimental T_{in} data (O) and the surface corresponding to the calculated T_{in} data (shaded) of MBPE-5/7/9(*A*/*B*/*C*). Arrows point to virtual T_{in} for homopolymers. (b) Experimental T_{ns} data (□) and the surface corresponding to the calculated T_{ns} data (shaded) of MBPE-5/7/9(*A*/*B*/*C*). Arrows point to virtual T_{ns} for homopolymers. (c) Experimental ΔH_{in} (O) and ΔH_{ns} (□) data and the surface corresponding to the calculated ΔH_{in} and ΔH_{ns} (shaded) data of MBPE-5/7/9(*A*/*B*/*C*). Arrows point to virtual ΔH_{in} and ΔH_{ns} for homopolymers.

Table III
Averaged and Virtual (in Brackets) Liquid Crystalline Transitions and the Corresponding Enthalpy Changes of MBPE-*X* As Determined from Binary (Ref 17) and Ternary (This Work) Copolymers

		thermal transitns (°C) and corresponding enthalpy changes (kcal/mol)	
polymer	data from	heating	cooling
MBPE-5	ref 17	s [44 ● 2 (0.14 ● 0.02)] n [60 ± 4 (0.43 ● 0.1)] i	2 51 (0.57) n 37 (0.10) s
	present	s [45 (0.13)] n [58 (0.4)] i	i 50 (0.46) n 37 (0.13) s
MBPE-7	ref 17	s [64 ● 4 (0.15 ± 0.04)] n [76 ● 4 (0.59 ± 0.12)] i	i [65 ● 1 (0.76 ± 0.04)] n [57 ● 2 (0.16 ● 0.05)] s
	present	s [61 (0.16)] n [73 (0.78)] i	i [66 (0.78)] n [56 (0.17)] s
MBPE-9	ref 17	s [71 ± 1 (0.14)] n [80 ● 7 (0.99 ± 0.10)] i	i 69 (1.05) n 58 (0.06) s
	present	s [67 (0.13)] n [77 (0.93)] i	i 70 (0.97) n 61 (0.12) s

Scheme I



phic or of the same type. However, the reverse is not true. When transplanted to copolymers, if the mesomorphic phase transition temperatures and thermodynamic parameters of copolymers represent weight-averaged values or at least continuous dependencies of the corresponding parameters of the parent homopolymers, then the mesomorphic phases of homopolymers and copolymers can be considered to be isomorphic or identical. Discrimination between miscible and isomorphic mesophases requires miscibility studies. For the particular copolymers described in this paper they are both miscible and isomorphic. Miscibility studies have shown that the nematic and smectic mesophases displayed by these three homopolymers and the corresponding copolymers are miscible. These results will be published elsewhere. However, this conclusion may not automatically apply to any copolymerization system. We have in progress investigations on copolymer systems of which mesomorphic phase transition temperatures and thermodynamic parameters display linear dependence of copolymer composition. However, the mesomorphic phases of their parent two homopolymers, although are identical, are not mis-

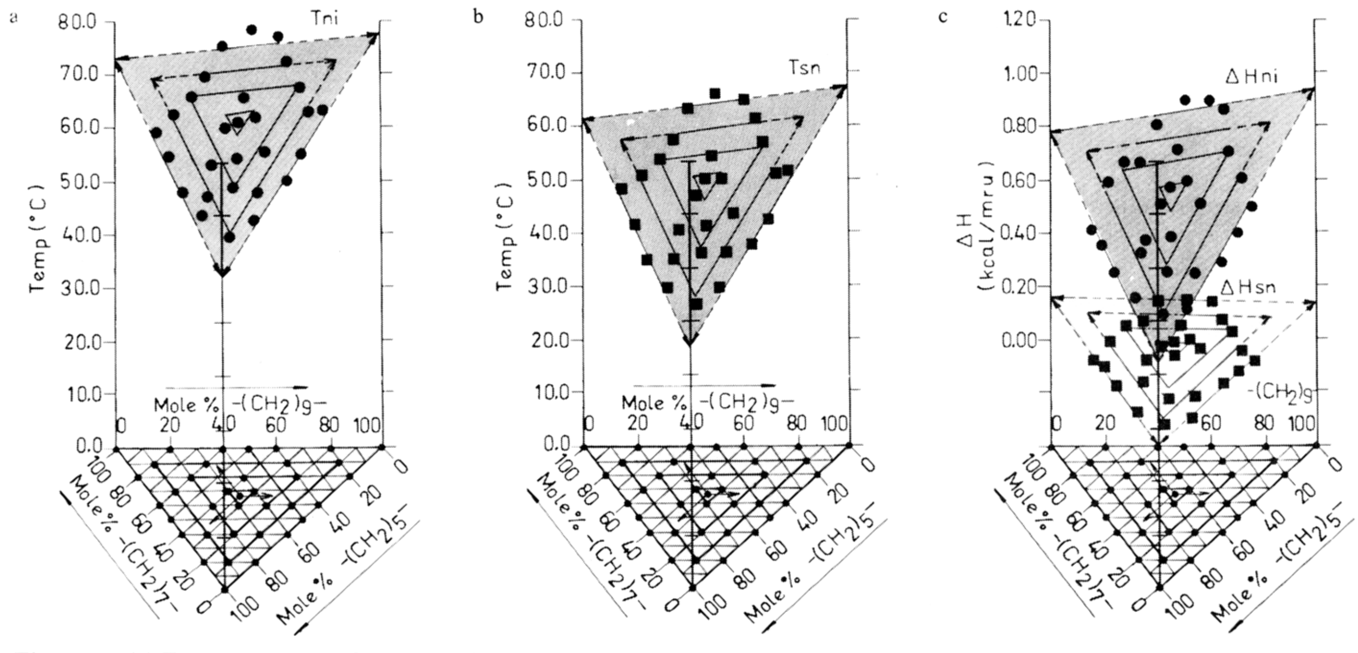


Figure 3. (a) Experimental T_{ni} data (●) and the surface corresponding to the calculated T_{ni} data (shaded) of MBPE-5/7/9(*A*/*B*/*C*). Arrows point to virtual T_{ni} for homopolymers. (b) Experimental T_{sn} data (■) and the surface corresponding to the calculated T_{sn} data (shaded) of MBPE-5/7/9(*A*/*B*/*C*). Arrows point to virtual T_{sn} for homopolymers. (c) Experimental ΔH_{ni} (●) and ΔH_{sn} (■) data and the surfaces corresponding to the calculated ΔH_{ni} and ΔH_{sn} (shaded) data of MBPE-5/7/9(*A*/*B*/*C*). Arrows point to virtual ΔH_{in} and ΔH_{ns} for homopolymers.

cible. We do not yet have information about the similar representations of copolymers based on a pair of nematic and smectic homopolymers. Nevertheless, it seems to be quite safe to consider at the present time that copolymerization is able to demonstrate at least whether the parent homopolymers display virtual liquid crystalline mesophases or not. The assignment of this mesophase may however require additional experiments. Subsequently, since copolymerization suppresses crystalline transitions, it provides the only method that can be used to determine virtual liquid crystalline transitions and the enthalpy changes of the homopolymers. This method represents the transplant of the use of low molar mass liquid crystal mixtures in the determination of virtual transitions[35,36] to the field of copolymers. Although miscibility studies between low molar mass liquid crystals and polymers have been extensively used to identify liquid crystalline mesophases displayed by polymers,[37] we are not aware of their use for the determination of virtual mesophases displayed by polymers.

So far this experiment was performed with main-chain liquid crystalline copolymers containing flexible spacers. Both binary[17-20] and ternary copolymers based on a certain mesogenic unit and two or three different flexible spacers follow this rule. Experiments with two different mesogenic units are in progress and will be reported soon. This rule is very important since by knowing the phase transition temperatures and the corresponding enthalpy changes of a series of homopolymers, by copolymerization we can design the mesomorphic–isotropic transition temperature and the degree of order displayed by the mesophase of the resulting copolymer. This paper demonstrated that this is indeed true at least for the present copolymers based on a single mesogenic unit and different flexible spacers.

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Registry No. MBPE-5, 115529-45-8; MBPE-7, 115529-46-9; MBPE-9, 115529-47-0; MBPE-5/7/9, 123725-16-6; MBPE-5/7, 115529-49-2; MBPE-7/9, 117068-61-8; MBPE-5/9, 117068-59-4.

References and Notes

(1) Ober, C. K.; Jin, J. I.; Lenz, R. W. *Adv. Polym. Sci.* **1984**, *59*, 103.
(2) Lenz, R. W. *Pure Appl. Chem.* **1985**, *57*, 1537.
(3) Lenz, R. W. *Polym. J.* **1985**, *17*, 105.
(4) Lenz, R. W. *J. Polym. Sci., Polym. Symp.* **1985**, *72*, 1.
(5) Lenz, R. W.; Jin, J. I.; Feichtinger, K. A. *Polymer* **1983**, *24*, 327.
(6) Chen, G.; Lenz, R. W. *Polymer* **1985**, *26*, 1307.
(7) Irwin, R. S.; Sweeny, W.; Gardner, K. H.; Gochanour, C. R.; Weinberg, M. *Macromolecules* **1989**, *22*, 1065.
(8) Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1987**, *188*, 1281.
(9) Kwolek, S. L.; Luise, R. R. *Macromolecules* **1986**, *19*, 1789.
(10) Harwood, H. J. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 331.
(11) Muhlbach, K.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2605.
(12) Auman, B. C.; Percec, V.; Schneider, H. A.; Jishan, W.; Cantow, H. J. *Polymer* **1987**, *28*, 119.
(13) Auman, B. C.; Percec, V.; Schneider, H. A.; Cantow, H. J. *Polymer* **1987**, *28*, 1407.
(14) Auman, B. C.; Percec, V. *Polymer* **1988**, *29*, 938.
(15) Percec, V. In *Phase Transfer Catalysis. New Chemistry, Catalysts and Applications*; Starks, C. M., Ed.; ACS Symposium Series 326, American Chemical Society: Washington, DC, 1987; p 96.
(16) Percec, V.; Yourd, R. *Macromolecules* **1988**, *21*, 3379.
(17) Percec, V.; Yourd, R. *Macromolecules* **1989**, *22*, 524.
(18) Percec, V.; Yourd, R. *Macromolecules* **1989**, *22*, 3229.
(19) Percec, V.; Yourd, R. *Makromol. Chem.*, in press.
(20) Percec, V.; Yourd, R. *Makromol. Chem.*, in press.
(21) Blumstein, A.; Vilagar, S.; Ponrathnam, S.; Clough, S. B.; Blumstein, R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 877.
(22) Roviello, A.; Santagata, S.; Sirigu, A. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 209.
(23) Watanabe, J.; Krigbaum, W. R. *Macromolecules* **1984**, *17*, 2288.

(24) Amendola, E.; Carfagna, C.; Roviello, A.; Santagata, S.; Sirigu, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 109.

(25) Fradet, A.; Heitz, W. *Makromol. Chem.* **1987**, *188*, 1233.

(26) Percec, V.; Nava, H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 405.

(27) Percec, V.; Nava, H.; Jonsson, H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 1943.

(28) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978.

(29) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals. Textures and Structures*; Leonard Hill: Glasgow and London, 1984.

(30) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill Book Co.: New York, 1969; p 164.

(31) Jurs, P. C. *Computer Software Applications in Chemistry*; Wiley: New York, 1986; p 53.

(32) Arnold, H.; Sackmann, H. *Z. Phys. Chem. (Leipzig)* **1960**, *213*, 1307.

(33) Arnold, H.; Sackmann, H. *Z. Phys. Chem. (Leipzig)* **1960**, *213*, 145.

(34) Sackmann, H.; Demus, D. *Mol. Cryst. Liq. Cryst.* **1973**, *21*, 239.

(35) Gray, G. W.; Mosley, A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 97.

(36) Domon, M.; Buisine, J. *Mol. Cryst. Liq. Cryst.* **1987**, *149*, 347.

(37) Noël, C. in *Polymeric Liquid Crystals*; Blumstein, A., Ed.; Plenum Press: New York, 1985; p 21.

Cyclopolymerization of Dipropargylgermaniums by Transition-Metal Catalysts

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ABSTRACT: Cyclopolymerization of dipropargylgermaniums $[(CH_3)_2Ge(CH_2C{\equiv}CH)_2$, $(Ph)_2Ge(CH_2C{\equiv}CH)_2]$ was examined for $MoCl_5$- and WCl_6-based catalysts. The WCl_6 and $MoCl_5$ catalysts are all effective in the polymerization of dipropargylgermaniums. Polymerization of diphenyldipropargylgermaniums by WCl_6 leads to soluble, highly colored polymers of a number-average molecular weight of ($\bar{M}_n$) 12 000. NMR (^1H and ^{13}C), IR, UV-visible spectroscopies showed that poly(diphenyldipropargylgermaniums) possess polyene structures having cyclic recurring units in the polymer backbone. Poly(dipropargylgermaniums) have been investigated in terms of physical properties, solubility, electrical conductivity, and thermal and oxidative stability. Fairly good thermal and oxidative stability and solubility of the present cyclopolymer are notable characteristics.

Introduction

Cyclopolymerization (ring-forming polymerization) is any type of chain growth addition polymerization that leads to the introduction of cyclic structures into the main chain of the polymer.[1]

Since the discovery of polymerization of 1,6-heptadiyne using Ziegler–Natta catalyst in 1961,[2] there have been many studies on the cyclopolymerization of nonconjugated diynes giving the conjugated double bonds in the polymer backbone and cyclic recurring unit. However, this catalyst leads to insoluble polymer films.[3] It was known that group VI metal-based catalysts exhibit a high catalytic activity for the polymerization of substituted acetylenes.[4] Recently, we have found that Mo- and W-based catalyst systems are very effective for the cyclopolymerization of dipropargyl sulfide,[5] dipropargyl ether,[6] and dipropargylsilanes.[7] The latter polymer is generally soluble, thermally stable, and has high electrical conductivity.

We have now investigated the cyclopolymerization of dipropargylgermaniums $[(CH_3)_2Ge(CH_2C{\equiv}CH)_2$, $(Ph)_2Ge(CH_2C{\equiv}CH)_2]$ by $MoCl_5$- or WCl_6-based catalysts. The physical and spectroscopic properties of the resulting polymer will be discussed.

Experimental Section

Monomers were prepared by a Grignard reaction.[8] Dimethyldipropargylgermanium (DMPGe), 1.22 mol of magnesium turnings, and 1.49 mol of propargyl bromide were reacted with 0.5 mol of dichlorodimethylgermanium. Yield: 66%. Bp: 70–72 °C (20 mmHg). Anal. Calcd for $C_8H_{12}Ge$: C, 53.15; H, 6.69. Found: C, 53.02; H, 6.47. ^1H NMR ($CDCl_3$): δ 0.40 (3 H, s, CH_3), 1.67 (2 H, d, $C{\equiv}CCH_2$), 1.90 (1 H, t, $C{\equiv}CH$). IR (NaCl): 3300, 2970, 2120 cm^{-1}.

Diphenyldipropargylgermanium (DPPGe). Yield: 60%. Bp: 104–106 °C (0.1 mmHg). Anal. Calcd for $C_{18}H_{16}Ge$: C, 70.90; H, 5.29. Found: C, 70.75; H, 5.11. ^1H NMR ($CDCl_3$): δ 7.2–7.7 (5 H, m, ArH), 1.90 (1 H, t, $C{\equiv}CH$), 2.27 (2 H, d, $C{\equiv}CCH_2$). IR (NaCl): 3310, 3100, 2910, 2120 cm^{-1}.

Polymerization. All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere. The cyclopolymers were synthesized by the same method as described in a previous paper.[7]

Polymer Characterization. ^1H NMR and ^{13}C NMR spectra were recorded with a Varian T-60A spectrometer and a Bruker AM-200 spectrometer. IR and UV–vis spectra were taken on a Perkin-Elmer 283B spectrometer and Cary 17 spectrometer. The number-average molecular weights ($\bar{M}_n$) of polymers were determined by GPC (150C of Waters) using a polystyrene calibration. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10 °C/min with a Du Pont 1090 analyzer. Thermal transitions were measured with a Du Pont 990 thermal analyzer. Electrical conductivities were measured by 2-point probe dc method with a Hewlett-Packard 6216A power supply and Keithley 485 picoammeter.

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