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Communications to the Editor

Gel Effect Leading to High Molecular Weight Side-Chain Liquid-Crystalline Polymers[1]

Introduction. The Trommsdorf effect is a well-known phenomenon in free-radical polymerization, particularly of vinyl and acrylate monomers.[2] This effect, also known as autoacceleration or the gel effect, has not been reported up to this time in syntheses of liquid-crystalline side-chain polymers. We report here on this phenomenon and its associated consequences in our polymerizations forming side-chain liquid-crystalline polymers. These polymers show narrowed thermal transitions and tougher film-forming properties than their lower molecular weight counterparts and therefore may have further applications.

Autoacceleration is observed in polymerization systems as the viscosity of the reaction mixture increases. The rate of termination by coupling decreases, since the free radicals cannot diffuse easily to each other, but the molecular weight continues to increase dramatically as monomer can still diffuse into the reactive chain ends. This produces high molecular weight polymer but with a skewed molecular weight distribution. Factors known to influence this phenomenon are temperature, medium viscosity, and polymer concentration.[3]

Side-chain liquid-crystal polymers (SCLCP's) have been the object of many investigations in recent years.[4-7] The syntheses as reported from acrylate or methacrylate monomers have been by free-radical methods in solution or by group-transfer polymerization.[8] Ziegler–Natta catalysis has been utilized to produce all-hydrocarbon SCLCP's.[9] Molecular weights have been reported ranging from $\bar{M}_w = 850\,000$[9] to 3200[10] and $\bar{M}_n = 133\,000$[11] to 2500,[12] as obtained by light-scattering or size-exclusion chromatography. Duran and Strazielle[10] have noted that molecular weights of SCLCP's obtained by size-exclusion chromatography coupled with light scattering are more than doubled compared to the molecular weights obtained on the same samples by SEC alone. They attributed this to the difference in hydrodynamic volume between the polymers and the standards (polystyrene).

Polymers have been made from the monomer 4 (Figure 1) under a variety of reaction conditions using AIBN as initiator. Similar polymers with the phenyl benzoate ester linkage reversed have been made by several groups.[12-15] The highest values of $\bar{M}_n$ quoted for these polymers are 43 000[12] (by vapor pressure osmometry) and 7200[13] (by SEC). Kostromin et al. gave $\bar{M}_w = 660\,000$ (by light scattering).[14] Keller made similar polymers by grafting the mesogenic group onto a polyacrylate backbone of average molecular weights 2100 and 6000.[17] The $\bar{M}_w$'s of the polymers presented here range from 7700 to 2 510 000 and the $\bar{M}_n$'s from 5700 to 1 044 000; when the gel effect is observed and under melt polymerization conditions, the molecular weight distribution is skewed and broadened (Figure 2). The broadness of the distribution may be controllable by the length of reaction time. Further investigation will be required to determine precisely protocols for control of polydispersity.

Experimental Section. The monomer was synthesized by the basic scheme given in Figure 1.

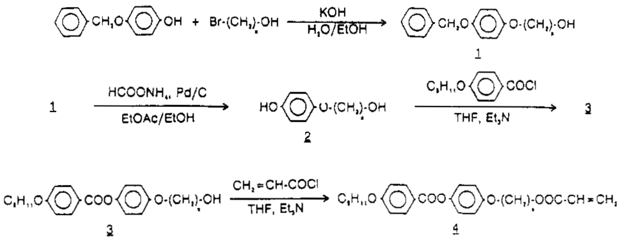

Figure 1. Synthetic scheme for monomer **4**, $x = 11$.

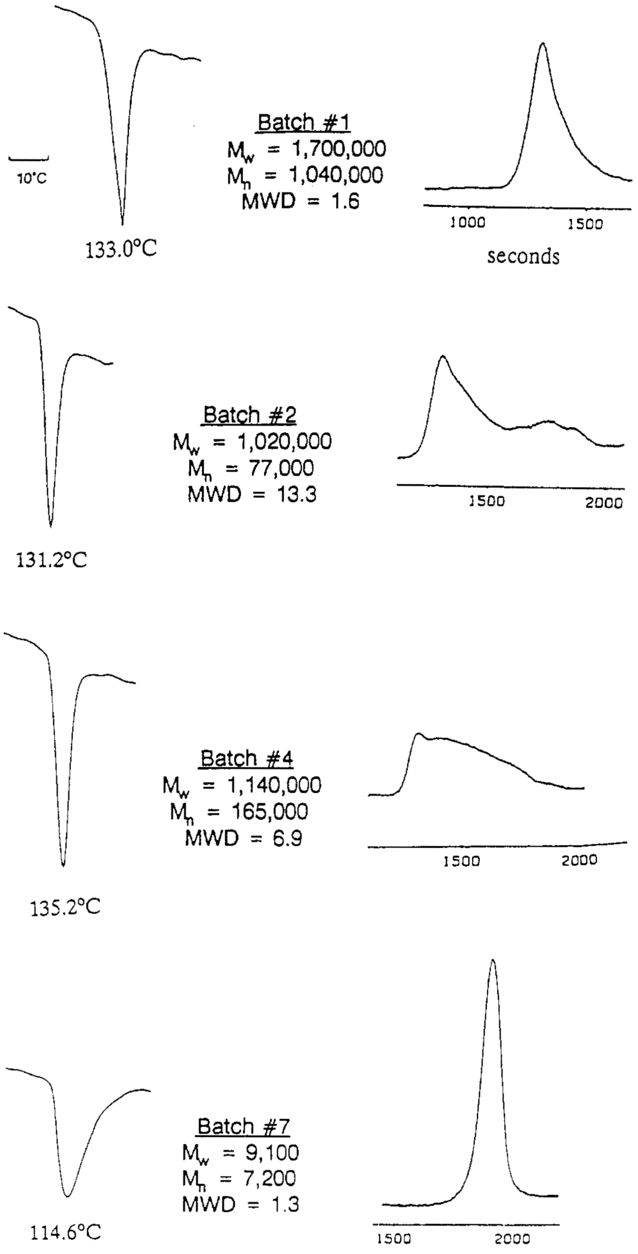

Figure 2. Size–exclusion chromatographs and liquid crystalline transitions by DSC for polymers. Batches: 1 and 2 = gel; 4 = melt; 7 = solution.

Thermal transitions of the monomer and polymers were measured on a Du Pont 9900 thermal analysis system using a Model 910 DSC cell at a heating rate of 10 °C/min under a flow of dry nitrogen. Optical textures were determined

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Table I
Transition Temperatures and Molecular Weights for Polymers

					transition temp, °C			
batch	method	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	MWD	g → S	S → S	S → S_A	S_A → I
1	1	17.1	10.4	1.6	54.4		79.1	133.0
2	1	10.2	0.77	13.3	53.7		77.3	131.2
3	1	25.1	10.4	2.4	52.9		78.1	130.0
4	2	11.4	1.7	6.9	56.2		76.8	135.2
5	2	6.2	0.75	8.2	51.2		76.6	134.0
6	2	13.8	2.4	5.8	53.1		73.8	128.9
7	3	0.091	0.072	1.3	46.4	58.2	71.0	114.6
8	3	0.078	0.057	1.4	48.8	59.5	69.0	117.1

using a Reichert Thermovar microscope with a Mettler FP5/52 programmable heating stage. Infrared spectra were obtained from a Mattson Polaris Fourier transform infrared spectrophotometer. ^{13}C NMR data were obtained on a Bruker MSL 200 equipped with a CP/MAS solids probe (field strength 4.7 T). A Hewlett-Packard 5985B gas chromatograph–mass spectrometer was used to obtain mass spectral data on the monomer. Relative molecular weights of the polymers were assessed by size-exclusion chromatography using a Waters system (6000A pump running at 1 mL of THF/min; 410 refractive index detector at 35 °C) equipped with four Waters Ultrastyragel columns of 100, 500, 10^4, and 10^5 Å against polystyrene standards.

11-[4-[[4′-(Pentyloxy)benzoyl]oxy]phenoxy]undecyl 2-Propenoate (4). First heat: K 60.0 I; subsequent heatings: K 50.9 N 60.0 I. MS: m/z 524 ($M^{\bullet+}$). IR (cm^{-1}): 1083, 1170, 1189, 1249, 1268, 1512, 1610, 1724, 2852, 2916, 2937. ^{13}C NMR (δ): 13.9 (CH_3), 22.3, 25.8, 25.9, 28.0, 28.4, 28.7, 29.1, 29.3 (aliphatic, m), 64.5 (CH_2OOC), 68.1, 68.2 (CH_2O-aromatic), 114.1, 114.9, 122.3, 132.0 (unsubstituted aromatic), 121.6, 144.3, 156.6, 163.3 (substituted aromatic), 165.0 (aromatic–COO–aromatic), 166.1 (acrylate COO), 128.6, 130.2 ($CH_2{=}CH-$).

All of the polymers showed similar spectral data. IR (cm^{-1}): 1076, 1168, 1198, 1255, 1511, 1607, 1735, 2852, 2921. ^{13}C NMR (δ): 13.9 (CH_3), 22.4, 25.9, 26.1, 28.1, 28.7, 28.8, 29.4, 29.6, 29.7 (aliphatic, m), 39.0, 41.7 (backbone), 64.6 (CH_2OOC), 68.3, 68.5 (CH_2O), 114.3, 115.0, 122.4, 132.2 (unsubstituted aromatic), 121.9, 144.5, 156.8, 163.4 (substituted aromatic), 165.1 (aromatic–COO–aromatic), 180.2 (acrylate COO).

Method 1. Gel. The monomer (0.5 g) was dissolved in a minimum of benzene (about 4 mL) in a round-bottomed flask. Dry nitrogen gas was introduced through a glass tube, and the flow continued throughout the reaction. The flask was immersed in an oil bath kept at 65 ± 2 °C. AIBN (1 mol %, 1.6 mg) was added as a solid, which immediately dissolved, and the mixture was stirred. After about 12 min, the volume of benzene had been greatly reduced, the solution had become a clear, colorless gel, and the stirrer could no longer stir; fibers could be pulled easily out of the gel. Heating at ~65 °C was continued for another 10 min. The reaction mixture was removed and dissolved in chloroform. The chloroform was evaporated and the polymer redissolved in toluene and precipitated twice with absolute ethanol (batch 1). Two more reactions were done under similar conditions and also produced gels. In the first (batch 2), gelation took place within 7 min and the mixture was removed immediately and dissolved in chloroform. In the second (batch 3), the gel had formed within 3 min and the reaction mixture was removed after a total of 5 min. Yield was about 20% of theoretical. The results are given in Table I.

Method 2. Melt. A solution of monomer (0.5 g) and 1 mol % AIBN (1.6 mg) was made in approximately 5 mL of dry, distilled benzene and mixed thoroughly. The benzene was removed under a stream of dry nitrogen gas. The solid mixture was powdered and placed in a glass polymerization tube. Vacuum was applied, and the tube was sealed with an oxygen torch. The tube was placed in a constant-temperature oven at 68 ± 1 °C. After about 15 min, the isotropic liquid had changed to a white solid that did not shift when the tube was tilted. The tube was heated for a total of 45 min. No fiber could be pulled from the solid without addition of solvent. The polymer was dissolved in chloroform to remove it from the tube. The chloroform was evaporated and the polymer precipitated three times from toluene with absolute ethanol (batch 4). Yields were about 70%. The experiment was repeated under similar conditions with a reaction time of 15 min (batch 5) and 20 h (batch 6). The results are also presented in Table I.

Method 3. Solution. A mixture of the monomer (0.5 g) and 1 mol % AIBN (1.6 mg) was placed in a polymerization tube and dissolved in a relatively large amount of dry, distilled benzene (about 40 mL/g of monomer). The benzene was degassed under vacuum, frozen, and thawed under vacuum three times. The tube was sealed with an oxygen torch under vacuum, placed in an oven kept at 75 ± 1 °C for 72 h, and then removed, and the benzene was evaporated. The polymer was precipitated three times from toluene with absolute ethanol (batch 7). Yields were near 80%. Another reaction was done under similar conditions (batch 8); the results are in Table I.

Results and Discussion. The polymers produced under the gelation conditions and under melt polymerization conditions showed very high molecular weights, higher than those reported up to this time for side-chain liquid-crystalline polymers. The polydispersity was very broad for the melt polymerizations, but for the reactions giving a gel effect, the polydispersity appears to be directly affected by reaction time and may be controllable in this way. The solution polymerizations showed a low polydispersity compared to the usual value of 2.0 for free-radical polymerizations, but the molecular weights were also low and these reactions do not proceed to completion.

The freeze–thaw technique was originally employed to minimize the effects of oxygen, which could cause cross-linking or termination. However, a study by Lee and Turner[18] on the value of $\bar{M}_v$ for polymers prepared in air or in vacuo found little difference between the two. This work involved polymers of methyl methacrylate using benzoyl peroxide as initiator; neat polymerizations showed the gel effect.

There is a definite increase in the S_A–I transition with increasing molecular weight (Table I). The degree of polymerization of 15–18, as found in the solution polymerizations, is not high enough to reach the plateau value for the S_A–I transition temperature. As higher molecular weights are reached, the transition temperatures are more constant and the transition widths as shown in Figure 2 are narrowed. Films from the polymers of higher molecular weights also show improved toughness compared to their lower molecular weight counterparts, which form rather brittle films.

The gel effect appears in our system to be a function of the viscosity of the reaction medium, as has been noted previously.[3] Gelation occurs as the volume of benzene is reduced, leaving viscous polymer and monomer with only a small amount of benzene (enough to keep the polymer in the form of a gel). Yields were quite low compared to the solution and melt methods, and this indicates that only a small amount of the monomer reacts to form the gel. Further experimentation on monomer types, reaction conditions, and controllability of the gel effect should permit a definitive statement on the polydispersities and molecular weights obtainable.

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