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Preparation of Liquid-Crystalline Side-Chain Polyacrylate by Chemically Modifying Poly(sodium acrylate) in Hexamethylphosphoramide

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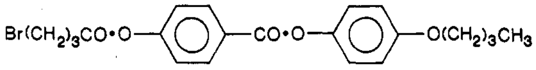
ABSTRACT: A new reaction scheme has been worked out for the synthesis of liquid-crystalline side-chain polyacrylate based on the chemical modification of poly(sodium acrylate) with a mesogen in hexamethylphosphoramide. The polymer product was characterized by IR and NMR spectroscopies for chemical structure, by GPC for molecular weight and its distribution, and by DSC and optical microscopy for thermotropic behavior.

I. Introduction

Because of the fundamental interest in liquid-crystal formation in polymeric systems and the potential for various technological applications, liquid-crystalline polymers have been the object of active research in recent years. Current advances in the synthesis and characterization and in empirical structure–property relationships are the subject of numerous monographs[1–4] and review articles.[5,6] There are basically two approaches to the synthesis of liquid-crystalline polymers: polymerization of liquid-crystalline monomers and chemical modification of polymeric substrates. The present work is on the chemical modification approach for two reasons. One is that this approach is attractive for its apparent simplicity, and the other is that reaction on polymers is another fascinating area of research in relation to polymer-supported catalysis.[7,8]

In the present study, we investigated the chemical modification of poly(sodium acrylate), PAA-Na, with a liquid-crystal mesogen, 4-butoxyphenyl 4-((4-bromobutanoyl)oxy)benzoate (**I**)

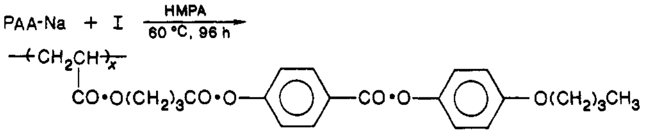


I

leading to a liquid-crystalline side-chain polymer. As detailed in a recent communication,[9] the liquid-liquid phase transfer reaction using tetrabutylammonium bromide resulted in an unexpected product. Instead of the anticipated polymer product,[10] a nucleophilic substitution reaction involving I initiated by the hydroxide ion present in the aqueous solution of PAA-Na yielded another low molecular mass liquid crystal. To avoid this problem, we looked into an alternative reaction scheme in which solid poly(sodium acrylate) is reacted with I in hexamethylphosphoramide (HMPA) in the absence of any phase transfer agent. Being a polar aprotic solvent, HMPA has been employed to carry out esterification of simple carboxylate salts[11–13] and other nucleophilic substitution reactions.[14–16] The resultant polymer liquid crystal is characterized by infrared (IR) and ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and hot-stage polarizing optical microscopy for mesophase identification.

II. Results and Discussion

The reaction between PAA-Na and I in HMPA is depicted as



II

A thin translucent film of product II, isolated and purified in accordance with the procedures stated in the Experimental Section, was cast on a sodium chloride plate from a chloroform solution for IR measurement. The spectrum presented in Figure 1 shows that the absorption due to the carboxylate group, a strong and broad band from 1550 to 1610 cm^{-1}, has disappeared. Furthermore, there is no unconverted carboxyl group either from the IR (2500 to 3000 cm^{-1}) spectrum or from the ^{1}H NMR (δ 10–15) spectrum. Hence, the conversion of carboxylate groups in PAA-Na to ester linkages to mesogen I appears to be complete. The relatively strong and sharp band at 1740 cm^{-1} is characteristic of the C=O stretching in an ester group.

The chemical purity of II was found to be better than 95% from GPC analysis. By use of the linear calibration curve established with five polystyrene standards with peak molecular weights from 503 to 35 000 g/mol, the number-average molecular weight ($\bar{M}_n$) was found to be 12 500 g/mol with a polydispersity factor of 1.15. Based on the average molecular weight of the poly(acrylic acid) used in the reaction, 2000 g/mol, the theoretical value for $\bar{M}_n$ was predicted to be 11 800 g/mol assuming complete conversion. The agreement between the two $\bar{M}_n$ values is reasonable although the GPC measurements have only a qualitative meaning. The ^{1}H NMR spectrum was also obtained to further verify the molecular structure of II. It is clear that the chemical shifts and spin–spin coupling patterns in Figure 2 are complicated by the polymer tacticity. On the basis of the spectrum obtained for I, we made peak assignment for protons designated as a–g. The signals for protons h and i tend to spread out between δ 1 and 3, as was observed for poly(acrylic acid).[17] Nonetheless, the molecular formula depicted as II appears to be consistent with the PMR spectrum.

Finally, the mesomorphic behavior was examined with DSC and hot-stage polarizing optical microscopy. Polymer liquid crystal II was found to exhibit a glass transition temperature around 56 °C an a clearing temperature around 120 °C as shown in Figure 3. As the polymer product was quenched from 160 °C in the atmosphere, the nematic threaded texture was observed under a polarizing microscope. The observation of the smectic (focal–conical) texture was accomplished by annealing the sample in an oven set at 80 °C for about 5 days. Hence, the clearing temperature observed on the DSC thermogram is pre-

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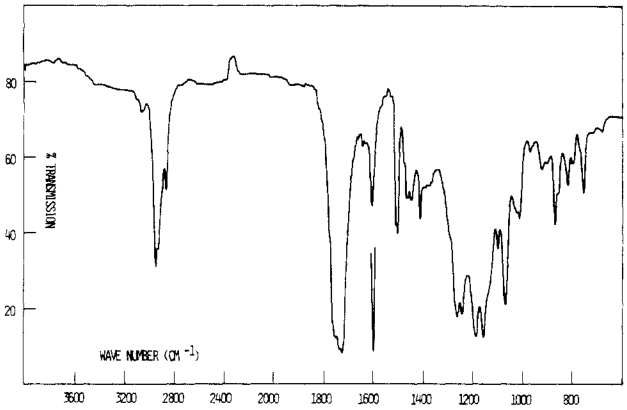

Figure 1. IR spectrum of polymer liquid crystal II obtained on a thin film cast on sodium chloride plate from chloroform solution and then dried in vacuum at 60 °C.

sumably associated with the nematic to isotropic transition, while the smectic to nematic transition is slightly above 80 °C although it is hardly identifiable on the DSC thermogram (Figure 3). Above all, the existence of both glass transition and clearing temperatures should suffice to claim the success in the preparation of a polymer liquid crystal by chemically modifying a polymeric nucleophile in an aprotic solvent in the absence of phase-transfer catalyst. We are currently working on reaction conditions that give rise to optimal yield of the polymer product.

III. Summary

The synthesis of liquid-crystalline side-chain polyacrylate was accomplished by chemically modifying poly(sodium acrylate) with a liquid-crystal mesogen in hexamethylphosphoramide without phase-transfer catalyst. The structure and mesomorphic behavior were characterized by IR and NMR spectroscopies, GPC, DSC, and optical microscopy. The reproducibility of the reaction was clearly demonstrated with repeated experimentation. The success of such a reaction scheme offers a unique opportunity for the chemical modification of polymeric nucleophiles without phase-transfer catalyst.

IV. Experimental Section

Synthesis of I. Liquid-crystal mesogen I was synthesized from *p*-hydroxybenzoic acid (99.5%, Kodak), *p*-butoxyphenol (99+%, Chemical Dynamics), and 4-bromobutyric acid (98%, Aldrich) following procedures reported by van Meter and Klanderman[18] and by Hassner and Alexanian.[19] The purity of I was found to be 97% based on GC analysis (GC 5890, Hewlett-Packard). The crystal to nematic and nematic to isotropic transition temperatures were determined to be 79 and 87 °C, respectively, using a differential scanning calorimeter (DSC-4, Perkin-Elmer) and a polarizing optical microscope (Leitz Orthoplan-Pol with Mettler FP52 Microthermal System). The structure of I was elucidated with IR (710B, Perkin-Elmer), NMR (300 MHz, QE-300, Nicolet), and mass (R10-10C, Nermag) spectroscopies.

Preparation of Poly(sodium acrylate). Poly(acrylic acid) with average molecular weight 2000 g/mol (65% solution in water, Aldrich) was neutralized with NaOH (10% in excess) solution. Poly(sodium acrylate) was then repeatedly precipitated from aqueous solution with methanol. The collected product was finally dried in vacuum at 60 °C for 4 days. The conversion of carboxyl to carboxylate group was verified with IR spectroscopy.

Preparation of II. Poly(sodium acrylate), 4.5 mmol, and mesogen I, 5.5 mmol, were placed in a round-bottom flask which contained 30 mL of hexamethylphosphoramide (99%, Aldrich). The mixture was stirred at 60 °C under N_2 atmosphere for 96 h. The suspended poly(sodium acrylate) could not be completely dissolved until 2 days later. At the end of the experiment, the reaction mixture was diluted with 150 mL of chloroform/diethyl ether (1:1) mixed solvent. The solution was then washed with distilled water (3 × 150 mL). The mixed solvent was then evaporated at reduced pressure, and the solid residue was dissolved in chloroform. After being dried over anhydrous sodium sulfate, the volume of the solution was reduced to about 5 mL under reduced pressure in a rotary evaporator, and the polymer liquid crystal (II) was precipitated 3 times from anhydrous diethyl ether. It is noted that precipitation in methanol gave colloidal dispersions from which product separation was very difficult to accomplish. The solid product was collected with a centrifuge, and the conversion was about 20%. Prior to analysis, the product was dried in vacuum at 60 °C for 4 days.

Thermal Characterization. The samples, I and II, for thermal analysis were heated to 250 °C and then quenched rapidly (at −320 °C/min) down to −50 °C prior to measurement on DSC-4 (Perkin-Elmer). The scan rate for the transition temperatures reported here was consistently 40 °C/min.

GPC Analysis. The GPC apparatus was constructed with an HPLC metering pump (Constametric III, Milton Roy), a column oven (Jones Chromatography), and a UV absorbance detector (UV III Monitor, Milton Roy) for detection at 254 nm. The calibration of the PL gel column (500 Å, Hewlett-Packard) was accomplished using a series of polystyrene standards (Pressure Chemicals) with the following peak molecular weights: 503, 2000, 4000, 17 500,

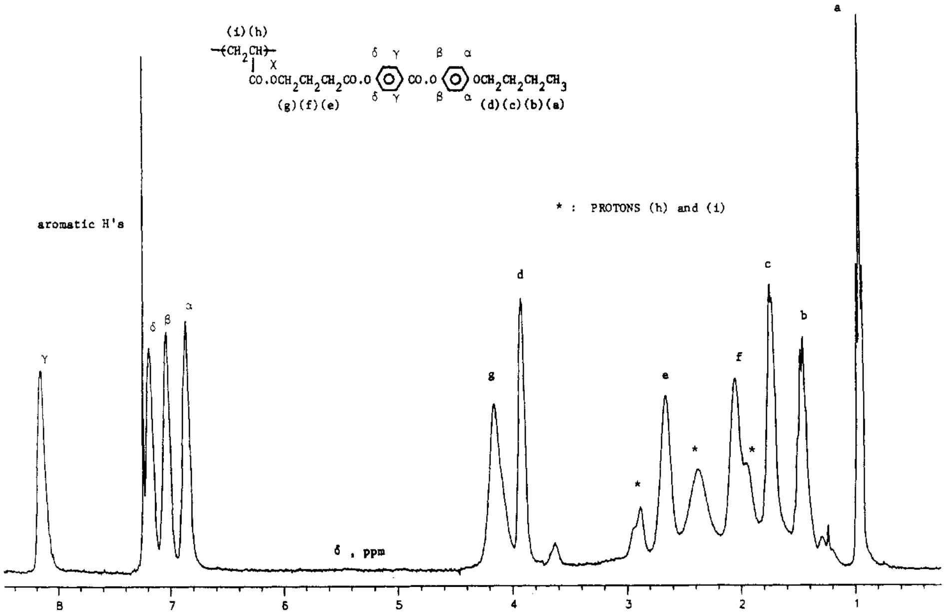

Figure 2. ^{1}H NMR (300-MHz) spectrum of polymer liquid crystal II, 2% by weight in $CDCl_3$.

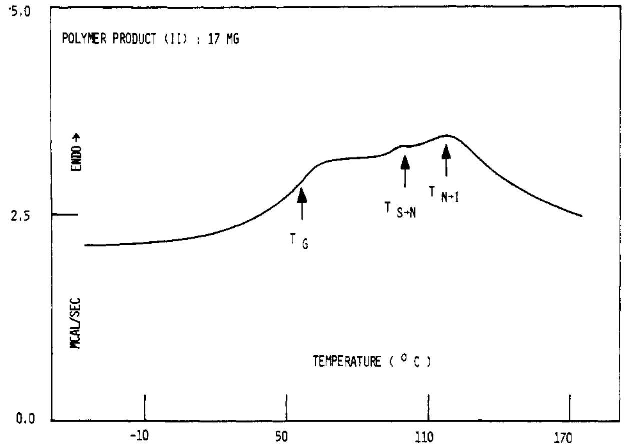

Figure 3. DSC thermogram of polymer liquid crystal II, scanned at +40 °C/min after quenching from 250 °C.

and 35 000 g/mol. The GPC trace was obtained for II in ethyl acetate (99.9+%, HPLC grade, Aldrich) at a column temperature of 40 °C and a flow rate of 0.84 mL/min. The linearity between the logarithm of molecular weight and retention volume for the polystyrene standards listed above justifies the reliability of the molecular weight distribution obtained for II from the GPC measurement; there should be no concern with the total exclusion of polymer solutes up to a molecular weight of 35 000 g/mol.

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Molecular Orientation Profiles in an Injection-Molded Liquid Crystalline Copolyester Characterized by Fourier Transform Infrared Attenuated Total Reflection Dichroism

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ABSTRACT: FT-IR ATR dichroism, averaging about 5 μm in depth, has been used to obtain the orientation profiles in injection-molded plaques of a thermotropic main-chain liquid crystalline polymer. The polymer is a copolyester containing 58 mol % of hydroxybenzoic acid (HBA) and 42 mol % 2,6-hydroxynaphthoic acid (HNA). Orientation functions were measured at eight positions as a function of distance from the end gate and at four positions in the thickness direction, providing a complex, three-dimensional orientation profile. Orientation profiles are similar for both HBA and HNA bands, a trend which attests to a random structure for this copolyester. Orientation functions along the surface plane show transverse orientation at a position closest to the gate due to the radial character of the flow in this region. Orientation functions in the thickness direction indicate that the chains are mostly planar with respect to the mold wall, especially on the skin. Based on the orientation data on the subskin, "the orientability parameter" was estimated to be close to unity, a value suggesting the enhanced orientational capabilities of these materials. The strong orientation of molecules in the skin layer generally decreases as one probes along the thickness direction. In the core layer, little orientation is observed in either the flow direction or the thickness direction for the first half of the mold, indicating random orientation probably due to the persistence of the polydomain structure in the molding operation. These experimental results are in agreement at least qualitatively with the predictions based on mold filling of short fiber-filled thermoplastics and structural rearrangements in liquid crystalline polymers.

Introduction

Recently, thermotropic main-chain liquid crystalline polymers (LCPs) have received a great deal of attention due to the possibility of melt processing these materials into products with exceptional physical properties. Researchers at Eastman Kodak were first to report on an aromatic–aliphatic copolyester made of *p*-hydroxybenzoic acid (HBA) and poly(ethylene terephthalate) (PET).[1,2]

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