Macromolecules 1985, *18*, 2331-2334

The Θ-condition results for PCEM yield a C_∞ value of 10.5. This value may be contrasted with those of 7.6–8.0 available[14-16] for poly(ethylmethacrylate) (PEM). Thus, the presence of the chlorine in the side chain influences the unperturbed chain dimensions of PCEM relative to PEM. A parallel effect of chlorine is seen for the case of atactic (in the Bernoullian sense) forms of poly(vinyl chloride)[17] and poly(propylene),[18] which possess characteristic ratios of 12 and 5.9, respectively, at nearly identical temperatures. Conversely, the unperturbed chain dimension behavior of poly(*p*-chlorostyrene) ($C_\infty = 10.6$)[19] demonstrates that the presence of chlorine exerts no influence (relative to polystyrene where $C_\infty = 10.7$[20,21]) when coupled with the relatively large and inflexible phenyl group.

The application of the rotational isomeric state model has shown,[22,23] the $\bar{g}$ conformations are virtually absent from poly(*n*-alkyl methacrylate) chains. The exclusion of the $\bar{g}$ conformers is the result of the planar nature of the ester group, which leads to potential steric overlaps involving one or the other oxygen atoms. This steric interference is not alleviated by an alteration of the rotational states of the neighboring bonds in the chain. Thus, *n*-alkyl methacrylate polymer chains are limited to the t and g forms as energetically accessible conformers. Our results for PCEM can be qualitatively interpreted relative to PEM, as a demonstration that the presence of the chlorine leads to an increase in the trans conformer content at the expense of the gauche conformer.

In conclusion, we wish to mention that our value of 67 (±2) °C for the glass transition is approximately 25 °C lower than the previous available value.[24] We only will note that our value for T_g is based on high molecular weight fractionated samples which did not contain residual solvent monomer or other plasticizing impurities. It is also germane to mention that poly(chloromethyl methacrylate) is reported[4] to have a T_g in the range 75–80 °C.

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Registry No. Poly(2-chloroethyl methacrylate) (homopolymer), 26937-47-3.

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Self-Polarizing Liquid Crystalline Films

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The theory of small-angle light scattering (SALS) from anisotropic solid materials has been described by Stein and co-workers on the basis of a model approach[1,2] as well as a statistical approach.[3,4] The former is useful for scatterers with known geometry such as spheres, disks, or rodlike structures. The latter represents a more general case without requiring any prior knowledge of the structures. SALS theory is commonly treated in various polarization configurations using a variety of combinations of a polarizer and an analyzer. These include Hv scattering (vertically polarized incident light with horizontal analyzer), Vv scattering (vertical polarizer with vertical analyzer), and Hh scattering (horizontal polarizer with horizontal analyzer).

SALS theory predicts that Hv scattering (under cross polarization) is primarily a result of orientation fluctuations while Vv scattering and Hh scattering (in parallel polarization) depend on additional contributions arising from density fluctuations as well as the polarizability of the surrounding medium. The theory has been rigorously applied to solid crystalline polymers[1-4] and recently to the superstructures forming liquid crystalline polymers.[5,6] The scattering of light from liquid crystals is found to be predominantly a consequence of orientation fluctuations. The intensity of this scattering turns out to be much greater than that arising from the density fluctuations in the nematic fluids, so much so that the latter contribution can practically be neglected. This is in accordance with the continuum theory of light scattering predicted by de Gennes.[7,8]

It is a common practice to utilize a combination of a polarizer and an analyzer in SALS experiments to specify the polarization directions of the incident electric vector and of the scattered wave. The present paper demonstrates that an anisotropic scattering pattern, characteristic of a rodlike scattering, can be obtained in a nematic liquid crystalline film without using an external polarizer or an analyzer. The material of interest is (hydroxypropyl)-

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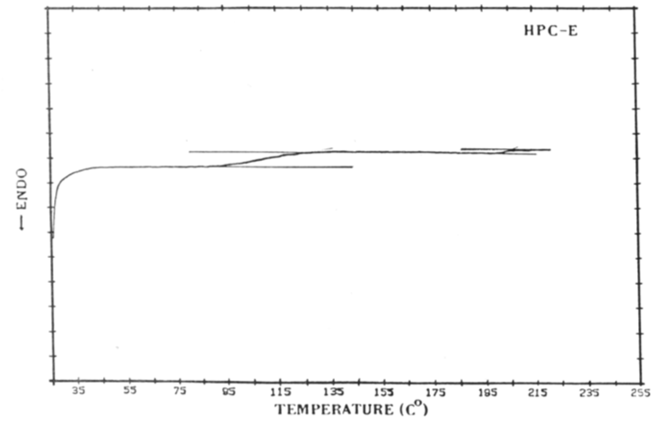

Figure 1. Differential scanning calorimetry (DSC) trace of compression-molded (hydroxypropyl)cellulose (HPC-E) film scanned at 10 °C/min.

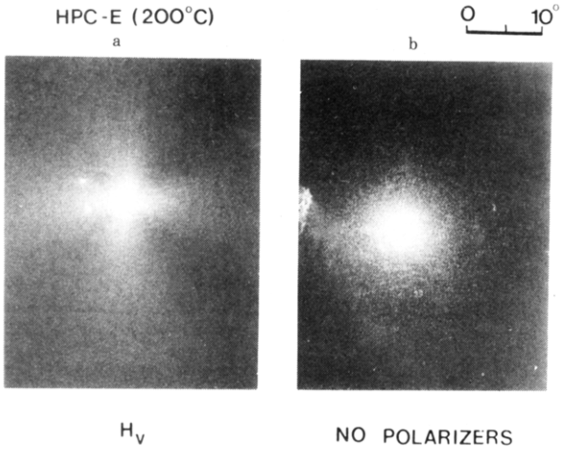

Figure 2. Light scattering pattern of (hydroxypropyl)cellulose film (HPC-E) squeezed at 200 °C: (a) under cross polarization (Hv scattering); (b) without polarizer or analyzer. (Vv scattering is similar to the scattering in (b).)

cellulose (HPC-E) with weight-average molecular weight (M_w) $\simeq$60 000 (Hercules Inc.). This material was initially considered to be a semicrystalline polymer.[9] This perception changed when Werbowyj and Gray[10,11] found that concentrated solutions of HPC exhibit lyotropic character in the presence of a selective solvent. It shows cholesteric mesophases at certain concentrations, displaying a color spectrum.[10,12] This material reveals thermotropic properties at elevated temperatures and is melt processable.[13]

The HPC disk samples (3-mm thickness and 25-mm diameter) are prepared by compression molding at 200 °C for 2 min at an elevated pressure. The melt samples are rapidly cooled to room temperature. Figure 1 shows the differential scanning calorimetry (DSC) trace of the compression-molded disk samples obtained at a heating rate of 10 °C/min. Transition regions appear in the vicinity of 110 °C and about 195 °C in the DSC thermogram. These transitions correspond to the solid–nematic transition and the nematic–isotropic transition, respectively.[14] The solid–nematic transition temperature can be affected easily by the presence of residual solvent or moisture; therefore the samples are carefully dried at 70 °C in a vacuum oven for a minimum of 24 h prior to the experiment. This thermotropic nematic region has been previously identified as a cholesteric mesophase.[13] The discrepancy may partly be due to the fact that the present material probably has not had time to achieve its equilibrium cholesteric structure during compression molding.

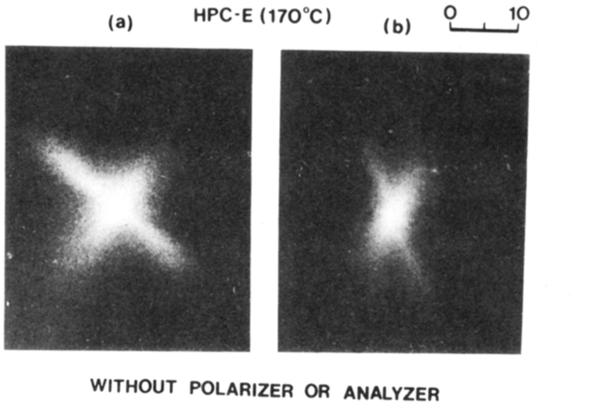

Figure 3. Light scattering pattern of (hydroxypropyl)cellulose film (HPC-E) squeezed at 170 °C: (a) near the center; (b) at the outer circumference. These SALS patterns are obtained without using any external polarizer or analyzer.

To obtain biaxially oriented thin films, the HPC disk is further squeezed at three temperatures (120, 170, and 200 °C). The squeezing temperatures approximately correspond to the solid–nematic transition, nematic mesophase, and nematic–isotropic transition regions. These squeezing temperatures are so chosen to examine the development of orientation and mesomorphic structures during the squeezing flow. The thickness of the squeezed film is reduced to 100 μm and the diameter is increased sixfold. These thin films are investigated by laser light scattering and polarized optical microscopy. A randomly polarized He–Ne laser light source with a wavelength of 6328 Å was used in the SALS experiments.

Figure 2 exhibits the SALS patterns of the HPC films squeezed at 200 °C with and without cross polarizers (Hv). A diffuse scattering pattern is observed when the polarizers are not used. Under Hv polarization, a typical rod-type scattering is seen which is generally observed in unoriented polycrystalline films, especially in poly(tetrafluoroethylene)[15] and HPC.[9] These observations are as expected because the squeezing temperature is already above the isotropic melt region.

A unique SALS observation has been made in the HPC film squeezed at 170 °C. Without requiring any polarizer or analyzer, a cross-type scattering pattern, reminiscent of typical rodlike scattering, is obtained as shown in Figure 3. This type of scattering is frequently observed in the Vv (or Hv) scattering of the oriented crystalline polymers.[15,16] The striking fact in this squeezed HPC film is that anisotropic rodlike scattering can be observed without using any external polarizer or analyzer. This strongly suggests the presence of self-contained polarizing layers of rod aggregates in the film plane. The polarization directions of these rod layers seem to be crossed to each other and vary through the film thickness. Since there is no scattering ring, characteristic of the cholesteric pitch, long-range order may not be present between layers of the rod aggregates. It is worth mentioning that the scattered intensity of one arm of the crossed scattering pattern is stronger than the other, reflecting the preferential orientation of the internal rods in one direction, probably in the tangential direction. The relative alignment of these rod-aggregate layers becomes more acute at the outer circumference of the squeezed film as compared to that near the center. This implies that the direction of these well-aligned rods of one layer orients relatively more parallel to those of the outer layer.

At a particular direction of the self-polarizing nematic rods the same scattering patterns can be observed in both

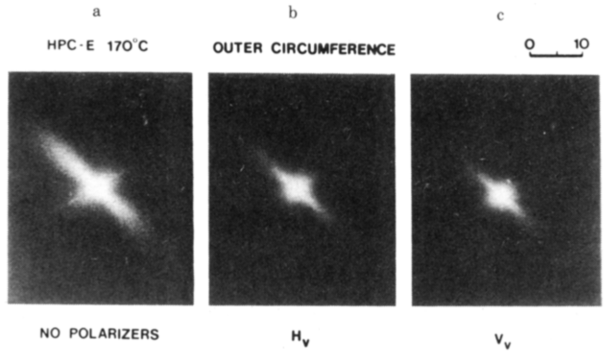

Figure 4. Light scattering pattern of (hydroxypropyl)cellulose film (HPC-E) squeezed at 170 °C: (a) without polarizer or analyzer; (b) Hv scattering; (c) Vv scattering taken at the outer circumference.

Hv and Vv scattering of this squeezed HPC film as shown in Figure 4. This is because the direction of polarized incident light has been altered when propagating through the self-contained polarizing planes of nematic rods. The anisotropic rodlike scattering pattern is thus largely determined by the internal polarization dependence of the scattering entities. Regardless of the position of the analyzer, the scattering pattern appears to be identical, leading to the fact that the configurations of external polarizers such as Hv and Vv polarizations are no longer significant. Similar observation is also made in the HPC films squeezed at 120 °C, but somewhat heterogeneous.

Figure 5 depicts the polarized optical micrographs focused at the film surface and at an intermediate layer of the above HPC films squeezed in the nematic mesophase. The direction of the well-aligned rod aggregates is perpendicular to that in the intermediate layers. The oriented rod layers align preferentially in the tangential direction at the film surface and at the bottom. This is probably associated with the shear flow at the walls of the squeezing plates. The intermediate layers consist of overlapping oriented rod aggregates in the tangential and radial directions, which may vary along with the radius of the film and also through the thickness directions. However, it should be mentioned that the rod orientation in the tangential direction is predominant over that in the radial direction at intermediate layers. This observation is consistent with the above SALS results. It seems that the outermost oriented surface and bottom layers may be serving as polarizing planes; therefore no external polarizer or analyzer is necessary in this particular SALS study. This observation indicates that the scattering from short-range orientation fluctuations of rod structures is predominant in the nematic mesophase.

The self-polarization effect by liquid crystalline polymers may not be surprising in view of the fact that optical anisotropy of rigid-rod molecules is extremely large, which gives rise to high scattering power. The incident light beam on entering such a film can easily be polarized as a result of the polarization dependence of these highly scattering entities. Even in conventional polymers such as polyethylenes, the polarization direction of the incident ray can be changed due to cascade scattering and can be scrambled out if the system is random or turbid.[17,18] This effect would be more accentuated in highly scattering systems such as liquid crystals. In this sense the phenomenon may belong to the class of multiple-scattering problems.[17] In the present case, however, the rod aggregates are aligned in a preferred direction, but varying from layer to layer; consequently, instead of being scrambled, the polarization direction alters in each layer due to the orientation of rodlike structures.

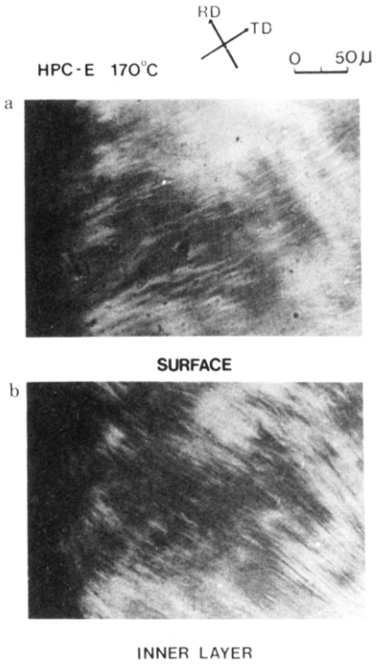

Figure 5. Polarized optical micrographs of (hydroxypropyl)cellulose film (HPC-E) squeezed at 170 °C: (a) at the surface; (b) at an intermediate layer taken near the center. The orientation direction of rod aggregates at the bottom is parallel to that at the surface.

If these rods are ideally aligned in one direction, the liquid crystalline film may possibly be used as an optical polarizer. This phenomenon is similar in character to the arrangement of iodine molecules in commercial polarizers and gold-grid infrared polarizers and also to radar technology. This will depend on the relative orientation, spacing, and size of the nematic rod structure. The control of structure development subject to flow or electric/magnetic field would undoubtedly be of crucial importance in the development of polarizer technology.[14]

In summary, we observed that self-polarizing layers of nematic rod aggregates are formed in squeezed HPC films. The squeezing flow in the nematic mesophase consists of radial and tangential flow of oriented nematic rods in layers. The mechanism of an oriented nematic rod structure formation seems to be associated with the rigidity of the macromolecules and the inability to pack a random arrangement of rods at moderate and high volume fractions. This formation was predicted by Flory[19] for concentrated solutions of rigid-rod molecules on the basis of a statistical thermodynamic consideration. It should be noted that the nematic rod structure of concern here is not a single rigid-rod molecule; it is a collection of well-aligned rigid molecules that formed a higher order rod structure. During the uniaxial flow in the nematic state, these rods tend to align with each other. The same argument should be valid in the biaxial squeezing flow, leading to formation of overlapping oriented nematic layers because a random arrangement of oriented rod aggregates in the same plane seems unfavorable.

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Registry No. (Hydroxypropyl)cellulose, 9004-64-2.

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Communications to the Editor

Heteronuclear Correlated Two-Dimensional NMR Spectroscopy Applied to the Diad Assignment of Vinyl Polymers

Nuclear magnetic resonance (NMR) spectroscopy has been widely used in past years as a practical method to analyze the configuration of polymers. Recently, two-dimensional (2D) NMR spectroscopy has been applied to this problem. Since 2D NMR experiments disperse the signals into two frequency domains, these techniques can, in principle, be used to resolve nearly degenerate resonances and make configurational assignments easier. For example, Bovey and co-workers[1] have used ^{19}F 2D *J*-correlated spectroscopy (COSY) to analyze the microstructure of poly(vinyl fluoride). Brown and co-workers have also made configurational assignments of poly(vinyl chloride)[2] and poly(vinyl alcohol)[3] by the use of ^{1}H 2D *J*-resolved experiments adapted for macromolecules (FOSY). Cheng and Lee[4] have employed ^{1}H–^{13}C heteronuclear shift-correlated 2D NMR (CSCM) to analyze the sequence distribution of ethylene–propylene copolymers. However, the use of this technique to study the configuration of polymers has not been reported. Recently, a broad-band homonuclear decoupling variation of the heteronuclear shift-correlated 2D NMR experiment (CSCMBB) has been proposed by Bax.[5] This experiment eliminates the coupling among vicinal protons in the ^{1}H domain and results in a contour plot with enhanced resolution and improved sensitivity. In this communication, we show that each of these experiments is extremely useful for the diad assignment of the methylene carbon of poly(vinylamine) (PVAm) and further suggest that these techniques may be general ones for making these assignments in other vinyl polymers.

Normally, the configurational assignments of resonances are made by comparing the polymer NMR spectrum to the spectra of model compounds or reference polymers, one with a dominant configuration. However, each of these methods is beset with difficulties. The use of model compounds may lead to wrong resonance assignments in the polymer spectrum when the polymer chemical shifts are influenced by long-range interactions and conformational effects not present in the models. Furthermore, reference polymers, if available, may have unique steric or conformational properties not present in atactic polymers which may result in chemical shift changes in certain resonances.[6] Certainly, it will be more desirable to make tacticity assignments strictly on the basis of the fundamental properties of the polymer in question. The 2D NMR approach described in this communication utilizes this feature.

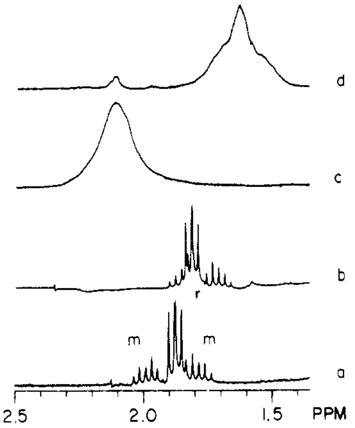
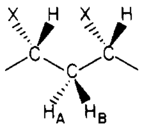
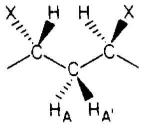


Figure 1. 300-MHz ^{1}H NMR spectra of 2,4-diaminopentane at pH 1.5 (a) and pH 8.8 (b) and of poly(vinylamine) at pH 1.5 (c) and pH 8.8 (d) in D_2O at room temperature. The 2,4-diaminopentane sample contained nearly a 1:2 mixture of meso and racemic isomers. The concentration of poly(vinylamine) was 0.05 M. Chemical shifts are referenced internally to 3-(trimethylsilyl)tetradeuterioproprionic acid sodium salt.

Results and Discussion. It has been known for years that the methylene protons of the meso (m) isomer for both model compounds and vinyl polymers are chemically nonequivalent and lead to two multiplets, while the methylene proton resonances of the racemic (r) isomer are degenerate.[6,7] For instance, the ^{1}H NMR spectra of 2,4-diaminopentane (DAP), in nearly a 1:2 molar mixture of m and r isomers at pH 1.5 (Figure 1a) and pH 8.8 (Figure 1b), illustrate these points. Two well-separated multiplets arise from the chemically nonequivalent methylene protons of *meso*-DAP. The central peaks are assigned to the methylene protons of *rac*-DAP. With increasing pH, the chemical shift difference between the two methylene m protons will become smaller but not vanish (Figure 1b). In principle, the nondegenerate methylene proton resonances can be used to determine the m and r content of vinyl polymers, as was recently shown for poly(acrylic acid)[8] as well as for other vinyl polymers.[6] Unfortunately, the ^{1}H NMR resonances of many vinyl polymers are ob-



meso diad



racemic diad

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