Macromolecules **1993,** *26,* 2413–2419

Thermodynamic Study of Ethylcellulose by Gas Chromatography

Jing-Yu Wang and Gérard Charlet*

Department of Chemistry and Centre de Recherches en Sciences et Ingénierie des Macromolécules (CERSIM), Université Laval, Cité Universitaire, Quebec City, Quebec, Canada G1K 7P4

Received July 27, 1992; Revised Manuscript Received January 21, 1993

ABSTRACT: The properties of ethylcellulose and its highly concentrated solutions with various chlorinated probes have been studied by inverse gas chromatography. The results show that the polymer cast at room temperature from solution is an orientationally ordered glass, where the chiral nematic structure, initially present in the liquid crystalline solution, has been kept upon drying. The cast samples experience a glass transition around 120 °C, but both the exact temperature and the width of the transition depend on the casting solvent and the thermal history of the sample. The excess enthalpy of mixing, calculated from the temperature dependence of the activity coefficients of the probe, is much more negative for the glass than for the polymeric liquid crystal above T_g and, therefore, is a sensitive indicator of the physical state of the stationary phase.

Introduction

Inverse gas chromatography (IGC) is widely used for the physicochemical characterization of macromolecules.[1-8] The properties which are commonly investigated by IGC include (i) structural features of the polymeric stationary phase, for example, its glass transition[1] or degree of crystallinity,[9] (ii) thermodynamics of polymer–solvent[1,10] and polymer–polymer mixtures,[11-13] and (iii) diffusion coefficients of volatile compounds in the polymeric matrix.[14,15] The IGC method is based on measurements on the retention time of a low molecular weight compound or *probe*. Most studies use parameters derived from the maximum of the concentration profile at the outlet of the chromatograph. This limits the measurements to a temperature range where the asymmetry of the chromatograms is presumably negligible, namely, about 50 °C higher than the glass transition of the stationary phase, T_g. Even at high temperature, however, the results often show a large dependence on the carrier gas flow rate, which raises question about their validity as equilibrium data. In a previous paper,[1] moment analysis was successfully applied to IGC: retention parameters based on the average residence time of the probe in the column, i.e., the center of mass of the elution profile, have been found to be independent of the carrier gas flow rate at temperatures as low as T_g.

In contrast with static methods such as osmometry or viscosimetry, IGC yields polymer–solvent interaction parameters at infinite dilution of the probe, i.e, at infinitely high concentration of the polymer. This feature is especially attractive for thermodynamic studies of solutions which form liquid crystals at high polymer content. Cellulose derivatives are one example of macromolecules which give rise to chiral nematic phases in solution.[16,17] The mesogens in such liquid crystals are essentially parallel except for a small twist in the orientation direction between neighboring molecules. This induces a supermolecular helical arrangement, whose periodicity or pitch is much longer than the molecular dimension. The occurrence of ordered phases in solutions of cellulosics is attributed to the lack of flexibility of the cellulose backbone. However, several phenomena, still not clearly understood, suggest that the solvent might play an active role. In the case of ethylcellulose (EC), for instance, the critical concentration, i.e, the minimum amount of polymer required at a given temperature for the onset of the mesophase, varies widely with the nature of the solvent. No evidence of liquid crystallinity has even been observed in some solvents.[18,19] Also, the handedness of the chiral liquid crystalline arrangement has been found to depend on the solvent.[19,20]

Thermodynamic studies of liquid crystals provide invaluable information on the origin of mesomorphic order and the nature of phase transitions.[21] The purpose of this work was to study EC and its solutions in various chlorinated solvents by IGC. A particular attention has been paid to the effect of the casting solvent and the thermal history on the structure and the thermodynamic properties of the stationary phase.

Data Reduction

The retention of a volatile probe on a stationary phase can be evaluated through the net retention volume, $V_N°$:

$$V_N° = \frac{t_p - t_m}{t_m} V_m \tag{1}$$

or the specific retention volume, $V_g°$:

$$V_g° = \frac{273.15}{Tm_2} \frac{t_p - t_m}{t_m} V_m \tag{2}$$

where T is the temperature, m_2 is the mass of the stationary phase, and t_p and t_m are the retention times of the probe and a noninteracting marker, respectively. The volume of the gas phase between the injector and the detector, or void volume, V_m, is a constant for a given packed column.[1] The mole fraction activity coefficient of the eluted component 1, at infinite dilution in the stationary component 2, is given by[22]

$$\ln\left(\frac{a_1}{x_1}\right)^{\infty} = \ln\left(\frac{RTn_2}{P_1°V_N°}\right) - \frac{P_1°(B_{11} - V_1)}{RT} \tag{3}$$

where n_2 is the number of moles of the stationary phase, $P_1°$, the vapor pressure of the probe, B_{11}, the second virial coefficient of the probe in the gas state, V_1, the molar volume of the probe in the liquid state, and R, the ideal gas constant. Other thermodynamic quantities which measure the change associated with mixing 1 mol of liquid probe with an infinite quantity of liquid stationary phase can be derived[23] from the activity coefficient, for instance, the excess enthalpy of mixing:

$$\Delta H_{\mathrm{m}}^{\infty} = R\frac{\partial \ln(a_1/x_1)^{\infty}}{\partial(1/T)} \tag{4}$$

The determination of (a_1/x_1) requires the knowledge of the molar mass of the stationary phase, which raises difficulties in the case of high molecular weight, polydisperse polymers. This prompted[22] the introduction of the weight fraction activity coefficient, which, at infinite dilution of the probe, reduces to

$$\left(\frac{a_1}{w_1}\right)^{\infty} = \left(\frac{a_1}{x_1}\right)^{\infty}\frac{\bar{M}_2}{M_1} \tag{5}$$

where M_1 and $\bar{M}_2$ are the molar masses of the probe and polymer, respectively. Equation 3 then changes to an expression which does not contain $\bar{M}_2$ explicitly:

$$\ln\left(\frac{a_1}{w_1}\right)^{\infty} = \ln\left(\frac{RTm_2}{P_1{}^{\circ}M_1V_{\mathrm{N}}{}^{\circ}}\right) - \frac{P_1{}^{\circ}(B_{11}-V_1)}{RT} \tag{6}$$

In order to derive meaningful retention times by moment analysis of the chromatograms, all extra-column contributions to peak broadening must be eliminated. A simplified chromatographic assembly, stripped from all connectors used for the measurement of the carrier gas flow rate, is required.[1] With such a setup, no determination of V_{m} can be performed. A value of $(a_1/w_1)^{\infty}$ relative to a constant is calculated merely from the retention times and parameters for the pure probe, using:

$$\ln\left[\left(\frac{a_1}{w_1}\right)^{\infty}\frac{V_{\mathrm{m}}}{V_0}\right] = \ln\left[\frac{RTm_2}{P_1{}^{\circ}M_1\left(\frac{t_{\mathrm{p}}-t_{\mathrm{m}}}{t_{\mathrm{m}}}\right)V_0}\right] - \frac{P_1{}^{\circ}(B_{11}-V_1)}{RT} \tag{7}$$

where V_0, an arbitrary constant with the dimensions of a volume, is introduced for consistency. The determination of activity coefficients relative to an unknown constant does not constitute a severe limitation of the IGC method, because the constant only depends on the column. Thus, the method allows for an accurate comparison between all the results acquired on a given column, e.g., for different probes or for different thermal and solvent histories of the stationary phase. Absolute values of the enthalpy of mixing are calculated from

$$\Delta H_{\mathrm{m}}^{\infty} = R\frac{\partial \ln\left[\left(\frac{a_1}{w_1}\right)^{\infty}\frac{V_{\mathrm{m}}}{V_0}\right]}{\partial(1/T)} \tag{8}$$

The above equations require some physicochemical parameters of the pure probes. In the present paper, the vapor pressures were calculated using the Antoine equation and constants taken from ref 24. The molar volume and second virial coefficient were estimated using the equations of Rackett or Van Ness, as described in ref 25. The arbitrary constant V_0 was taken as 1 cm^3.

Experimental Section

Materials. Ethylcellulose was a commercial sample purchased from Aldrich Chemical Co. The nominal ethoxy content was 48%, giving a degree of substitution (i.e., the average number of oxygens of the original cellulose repeat unit, now bearing a substituent) slightly inferior to 2.5. The weight-average molecular weight and polydispersity were determined to be 325 000 and 2.0, respectively, by size-exclusion chromatography. The chromatographic support was Chromosorb W (acid-washed and treated with dimethylchlorosilane), obtained from Chromatographic Specialty Inc. This support was chosen after preliminary studies[15] on columns packed with various pure supports. Only Chromosorb W exhibited negligible retention of chlorinated probes at temperatures as low as 70 °C. Three compounds were used both as casting solvents for the stationary phase and injected probes: chloroform, dichloromethane, and 1,1,1-trichloroethane (Aldrich Chemical Co.). They were at least 99% pure and used without further purification.

Table I. Experimental Characteristics of the Columns and the Chromatographs

column	material	i.d. (cm)	length (m)	m_2[a] (g)	loading[b] (%)	chromatograph
I	stainless steel	0.256	3.00	0.2573	8.14	Varian 3300
II	copper	0.483	1.85	0.4963	4.76	Hewlett-Packard 7620A

[a] Mass of the polymer in the column. [b] Weight ratio of the polymer in the chromatographic support.

Chromatography. The chromatographic support was coated with EC using a solution in dichloromethane (about 2% by weight) and a method which allows for the determination of the accurate content of polymer on the support, as previously described.[1] Two packed columns were used in two different chromatographs in this work. The detailed characteristics of instruments and columns are given in Table I. Both chromatographs were equipped with a flame ionization detector (FID). Dried helium was the carrier gas, while methane served as a marker to evaluate t_{m}, the time required to cover the distance between the injector and detector in the absence of any retention. Detector and injector temperatures were 210 and 185 °C, respectively. A simplified IGC assembly, composed of only the injector, the column, and the detector was used in both chromatographs, so that a statistical moment analysis of the chromatograms could be performed. The retention times were estimated from the first moment of the elution profiles. The ratio $(t_{\mathrm{p}} - t_{\mathrm{m}})/t_{\mathrm{m}}$ was then independent of the flow rate and size of injection (between 2 and 40 μL of vapor) over the entire temperature range investigated. For a stationary phase of given thermal and solvent histories, the retention parameters were measured twice at several temperatures upon cooling, first from 93 to 70 °C after annealing at 95 °C and then from 171 to 70 °C after annealing at 175 °C. Annealing times were never less than 6 days. At least two measurements of the retention times of the probe and marker were performed at each temperature.

Preparation of Polymer Films. Free-standing EC films were cast from solutions in chloroform, dichloromethane, and 1,1,1-trichloroethane. Direct mixing of EC and solvent was avoided in order to prevent contamination of the final polymer film with low-boiling impurities from the solvent, which would act as plasticizers. The following procedure was used instead. Known amounts of solvent and as-received polymer powder (volume ratio about 10:1) were placed in separate vessels in the same container. The air was removed from the latter, which was then closed. After a few days, all solvent was found to have transferred to the polymer vessel, forming a homogeneous solution. The solvent was slowly evaporated at room temperature, first under a partial pressure of solvent vapor slightly lower than the saturated pressure and then under vacuum. The evaporation was performed as slowly as possible, over several days, in order to allow the solution of changing concentration to remain at equilibrium.

Preparation of the Stationary Phase. In order to study the effect of the casting solvent on the resulting properties of the polymer film, a new method was designed to reproduce the casting conditions in the chromatographic column itself. The main benefit of the method is to allow for the study of different casting solvents on the same column, therefore keeping instrumental parameters, such as the amount of the polymer or the volume of the gas phase in the column, constant. The column was connected to a saturator containing about 20 mL of the casting solvent. Nitrogen was bubbled in the solvent at room temperature and a flow rate of 1 mL min^{-1}, until all solvent had been driven into the column, which took about 2 weeks. The column was left

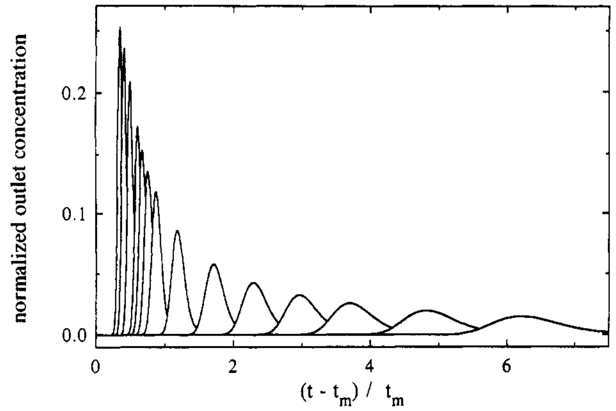

Figure 1. Elution profiles of chloroform on ethylcellulose at different temperatures: (from left to right): 166, 156, 146, 136, 130, 125, 120, 110, 100, 93, 87, 82, 77, and 72 °C. The stationary phase was cast from a chloroform solution. The time scale is relative to t_m, the retention time of the methane marker. The detector signal has been normalized by dividing each height by the surface of the chromatogram.

connected to the same assembly under the flow of nitrogen for several days in order to slowly dry the stationary phase. The column was finally placed in the chromatograph for conditioning by a gradual increase of the temperature over 6–8 days. After the retention measurements were completed, the procedure was repeated on the same column, in order to prepare another stationary phase using a different casting solvent.

Calorimetry. The heat capacity of EC films was measured in an adiabatic Calvet scanning calorimeter (C-80, SETARAM, Lyon, France). Measurements were performed upon heating at a rate of 0.1 °C min^{-1} between 30 and 180 °C. No data could be collected at higher temperatures, due to the degradation of the polymer occurring at low heating rates, i.e., long residence times.

Dynamic Mechanical Thermal Analysis (DMTA). The elasticity modulus (E') and loss tangent (tan δ) of EC cast films were determined using a dynamic mechanical thermal analyzer (Polymer Laboratories, Inc.). The measurements were performed on rectangular specimens (about 3 × 0.7 × 0.2 cm^3) in the cantilever bending mode, using five frequencies (0.3, 1, 3, 10, and 30 Hz). The results reported in Figures 3 and 5 were obtained at 1 Hz. Two scans were recorded upon heating at 1 °C min^{-1}, first from 60 to 170 °C and then from 60 to 230 °C. A flow of nitrogen was maintained on the sample throughout the experiments.

Polarized Optical Microscopy. The intensity of white light, transmitted by the cast films when placed between crossed polarizers, was measured by microscopy (Zeiss Standard, West Germany). The films were heated under nitrogen at 1 °C min^{-1} in a Mettler FP800 hot stage.

X-ray Diffraction. Wide-angle diffraction spectra were obtained from free-standing samples, using nickel-filtered Cu Kα radiation (λ = 0.154 418 7 nm) produced by a Rigaku RU-200BH rotating-anode X-ray generator operated at 50 kV and 160 mA. Collimation of the incident beam was achieved through a Soller slit and a 2.0-mm pinhole. All scans were recorded in the symmetrical transmission geometry, the normal to the sample being positioned at angle θ with respect to the incident beam while the diffracted intensity was measured at 2θ by a detector equipped with a pulse-height analyzer.

Results and Discussion

Thermal Transition in Ethylcellulose. Nature of the Transition. Figure 1 gives the chromatograms of chloroform recorded on EC upon cooling from 175 °C. The profiles are narrow and symmetrical at high temperature but widen at temperatures lower than about 110 °C. Also the temperature dependence of the retention time increases at low temperature. Similar features are observed when dichloromethane or 1,1,1-trichloroethane is used as the probe. The effect is indicative of a transition in the stationary phase. It is different from the change in the shape of the elution profiles observed upon cooling an amorphous polymer below its glass transition. Resistance to mass transfer is less affected by the transition in EC than by a conventional glass transition, since no sudden decrease in the position of the peak maxima occurs.[26] The relative activity coefficients of various probes in EC cast from various solvents have been calculated from the retention times, using eq 7. Plots as a function of reciprocal temperature are given in Figure 2. For all systems, two linear regions are observed. The transition temperature from one region to the other does not vary with the probe, since the lines intersect at about the same temperature for a given stationary phase. Again, this suggests the occurrence of a transition in the polymer itself. A similar discontinuity could be observed on retention diagrams, e.g., plots of $\ln(V_N{}^\circ/V_m)$ as a function of reciprocal temperature. In order to ascertain the nature of the transition, the dynamic mechanical properties of cast films of EC were studied as a function of temperature. The results are presented in Figure 3. The elastic modulus, E', shows a rapid decrease at about the same temperature as the change of slope in the plots of Figure 2. Figure 3 shows that, as E' decreases, the ratio of storage to elastic moduli, or loss tangent, goes through a maximum. The temperature of this maximum was observed to vary linearly with the logarithm of the frequency of deformation, increasing by about 5 °C for every 10-fold increase of the frequency. These mechanical properties are typical of a glass transition. The heat capacity of the films was measured as a function of temperature by scanning microcalorimetry. The plots have been drawn in Figure 3 for comparison. They show that the transition is second-

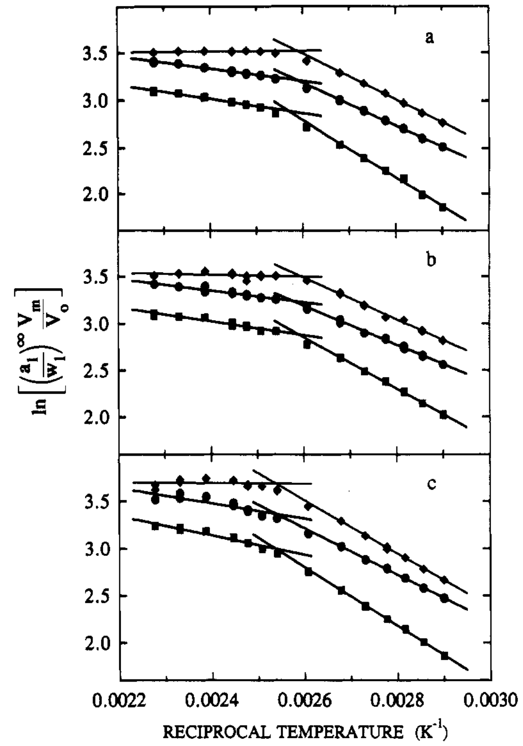

Figure 2. Effect of temperature on the relative activity coefficients of chloroform (■), dichloromethane (●), and 1,1,1-trichloroethane (◆) at infinite dilution in ethylcellulose. The same column was used with stationary phases cast from (a) chloroform, (b) 1,1,1-trichloroethane, or (c) dichloromethane and annealed at 175 °C. The solid lines are the results of a least-squares regression applied on data gathered at either the six lowest or the six highest temperatures. The transition occurs at a temperature which does not depend on the probe but varies with the casting solvent.

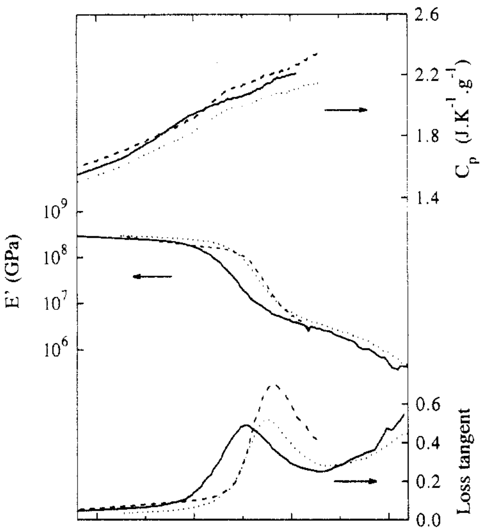

Figure 3. Dynamic mechanical properties and heat capacity of ethylcellulose as a function of temperature. The samples were cast from dilute solutions in 1,1,1-trichloroethane (full line), chloroform (dashed line), or dichloromethane (dotted line) and annealed at 175 °C prior to the measurements. The heat capacity, C_P, the elastic modulus E', and the loss tangent, E''/E', exhibit the characteristic features of a glass transition. However, the DMTA results show that the width of the transition depends on the casting solvent.

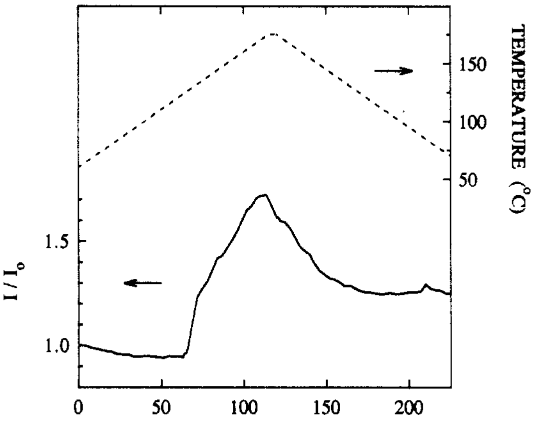

Figure 4. Effect of thermal history on the birefringence of a film cast from CH_2Cl_2. The intensity of light, I/I_0 (full line), transmitted by the film when placed between crossed polarizers, has been measured as the temperature (dashed line) was first increased from 70 to 175 °C and then decreased back to room temperature at a rate of 1 °C min^{-1}. Similar behaviors were observed for the films cast from $CHCl_3$ or CH_3CCl_3.

order. The changes in heat capacity, ΔC_P, are between 0.17 and 0.28 J g^{-1} K^{-1}, i.e., between 40 and 65 J K^{-1} mol^{-1}. Again, this is consistent with a glass transition involving a polymer constituted of large rings as repeating units.[27] All EC films cast from chlorinated alkanes at room temperature exhibited birefringence at room temperature. Figure 4 shows the temperature variation of the light intensity transmitted by such a film, when observed between crossed polarizers under an optical microscope. Upon heating (left part of the figure), the intensity remains constant until the transition temperature. The birefringence then increases sharply. If heating is continued further (not shown in the figure), a slow decrease is observed from 180 °C and the last trace of birefringence disappears around 240 °C. Similar observations[28] on samples of unspecified history led to the conclusion that ethylcellulose forms a thermotropic liquid crystal. Therefore, the transition observed in Figures 2 and 3 can be attributed to a glass transition where the solid at low temperature is not amorphous but contains orientational order and converts to a liquid crystal upon devitrification. At room temperature, EC cast films belong to the same class of materials as glasses obtained by cooling a liquid crystal, or LC glasses.[29] For the latter, the presence of the mesophase was found[27] to have no influence on the various features of the glass transition. The presence of orientational order in EC films cast from a dilute isotropic solution can be explained as follows: concentrated solutions in the casting solvents are chiral nematic. Upon slow evaporation of the solvent at room temperature, the polymer concentration increases until the critical value for liquid crystal formation. The latter is about 30–40% (w/w) in chlorinated alkanes. Upon further drying, the concentration of the ordered solution increases until the viscosity is such that the polymer chains lose mobility. This corresponds to crossing the glass transition temperature–composition curve. The complete evaporation does not induce any further change in the polymer arrangement.

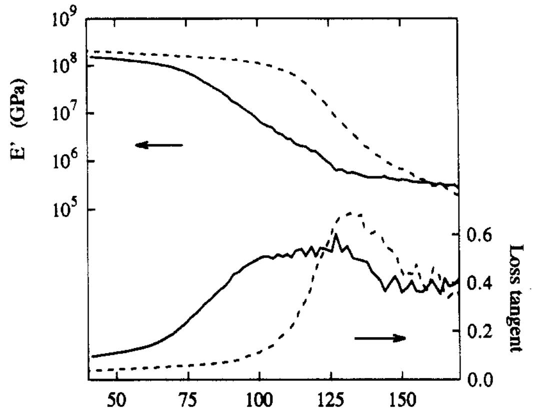

Figure 5. Effect of thermal history on the dynamic mechanical properties of EC cast from 1,1,1-trichloroethane. The measurements were performed with a frequency of deformation of 1 Hz and at a heating rate of 1 °C min^{-1}. The glass transition occurs at a higher temperature and over a shorter temperature range upon the second heating (dashed line) than the first (solid line). The results are similar when other solvents are used to cast the film, although the effect is the largest for CH_3CCl_3.

Effect of Thermal History. The results of Figures 2 and 3 were obtained on cast films (either the stationary phase in the column or a free-standing sample) that had been annealed at 175 °C. The properties of the films upon the first heating after casting at room temperature are different, as shown, for instance, in Figure 4. As already mentioned, the birefringence is constant for the glassy film but increases with temperature above the glass transition. The phenomenon is essentially reversible upon cooling the film back from 175 °C to room temperature, except for a significant increase of the birefringence of the glass. The mechanical properties are also affected by the thermal history of the sample. Figure 5 shows the results obtained by DMTA on a sample cast from 1,1,1-trichloroethane. The comparison of the mechanical properties measured upon the first and the second heating reveals that annealing promotes an increase of the glass transition temperature, T_g, by almost 20 °C. Also, the transition is sharper and the elastic modulus is higher for the annealed glass than for the original cast film. In order to understand the changes prompted by annealing above T_g, the heat capacity of cast films was measured upon their first heating. The results are shown in Figure 6. In contrast with the calorimetric traces recorded for annealed samples (Figure

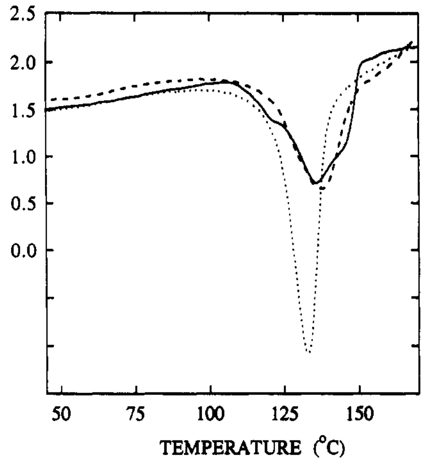

Figure 6. Heat capacity of EC cast films, recorded upon heating for the first time after casting at room temperature. The films were prepared from solutions in 1,1,1-trichloroethane (solid line), chloroform (dashed line), or dichloromethane (dotted line).

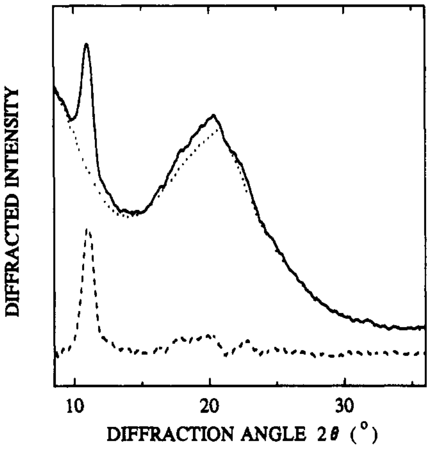

Figure 7. Wide-angle X-ray diffraction patterns of an ethylcellulose cast film. Diagrams were recorded before (dotted line) and after (full line) annealing at 175 °C. The dashed line represents the subtraction of the two curves.

Table II. Glass Transition Temperature of Ethylcellulose as a Function of Thermal History and Casting Solvent

	T_g (°C)			
		annealed[b]		
	as-cast:[a] DMTA[c]	DMTA[c]	C_p[d]	IGC[e]
cast from $CHCl_3$	134	142	117	115
cast from CH_3CCl_3	117	129	101	113
cast from CH_2Cl_2	134	138	116	121

[a] The polymer samples were cast at room temperature from dilute solutions, as described in the Experimental Section. The rate of evaporation of the solvent was kept as low as possible, in order to ensure that the solution reached equilibrium at all concentrations. T_g was then measured upon the first heating. [b] The samples were annealed at 175 °C, for times varying between a few hours for the films used in the mechanical property measurements and a few days for the stationary phases in the chromatograph. [c] T_g was taken as the temperature of the maximum of the loss tangent, measured at a frequency of deformation of 1 Hz and a heating rate of 1 °C min^{-1}, as shown in Figures 3 and 4. [d] The glass transition was taken as the lowest temperature at which the polymer is a pure liquid, i.e., at the upper limit of the transition range (Figure 3). [e] As shown in Figure 2, T_g can be determined from the change in the variation of the relative activity coefficients with temperature. Within the 95% confidence interval on the linear regression parameters, the transition temperature is independent of the probe injected. The values listed are averages for the three probes.

3), an exotherm is observed when cast films are heated above T_g for the first time.[30] The effect is the same for all cast films, although the change of enthalpy depends on the casting solvent, ranging from −29.1 to −43.4 J g^{-1}, i.e., from −6.73 to −10.0 kJ/mol of repeat unit. Exothermic phenomena at T_g are generally associated with crystallization. Wide-angle X-ray diffraction measurements were therefore performed on EC cast films before and after annealing. Figure 7 shows the diffraction patterns for a sample cast from a trichloroethane solution. The as-cast samples (dotted line) are characterized by a wide halo centered around $2\theta \simeq 21°$, corresponding to a distance of about 4.2 Å. New reflections appear upon annealing (solid line), as emphasized by the subtraction of the diagrams for the annealed and pristine films (dashed line). The degree of crystallinity of the film cast from CH_3CCl_3, assessed from the ratio of the areas of crystalline peaks and an amorphous halo, is on the order of 12%. The large exothermic heats observed in Figure 6 are unlikely to originate from recrystallization alone, since the enthalpy of fusion of the fully crystalline polymer would then be about 0.25 kJ g^{-1} or 59 kJ mol^{-1}. This value would the highest reported for a polymer so far, higher than the heat of fusion of polyethylene or polyesters.[31] The enthalpy released at T_g reflects an overall increase in the degree of order in the polymer, which originates not only from recrystallization but also probably from an improved alignment of the chains into the chiral nematic arrangement of the liquid crystal. An exotherm was shown[32] to accompany the transition from an amorphous state to a nematic phase at T_g in a side-chain liquid crystalline polymer. It is not possible to assess the relative importance of recrystallization and increase in orientational order in the effect of thermal history. Both factors increase the transition temperature, the elastic modulus, and the birefringence of the glass. Table II summarizes the effect of thermal history on the glass transition temperature of EC, as measured by various techniques. The agreement between the results is good, considering that T_g measured by dynamic methods is normally higher than that measured by static methods.

Effect of the Casting Solvent. An increase in T_g upon annealing is observed for all cast films. However, the transition temperature itself, as well as the extent of the effect of thermal history, depends on the casting solvent. For instance, the glass transition temperature of annealed samples, determined from Figure 2, is 113, 121, or 115 °C, depending on whether the film was cast from a solution in 1,1,1-trichloroethane, dichloromethane, or chloroform, respectively. The differences are more pronounced between T_g measured in the course of the first heating of the films, as shown in Table II. A difference as high as 17 °C is observed between the glass transition temperatures of films cast from 1,1,1-trichloroethane and from chloroform or dichloromethane. As already discussed, the orientational order in the cast films originates from the liquid crystalline arrangement present in the casting solution when crossing the T_g–composition curve upon drying. The effect of casting solvent indicates that both the chiral nematic pitch and the glass transition temperature of the solution vary differently with concentration in the various solvents.

Excess Enthalpy of Mixing. The retention data allow us to calculate thermodynamic functions which measure the effect of mixing 1 mol of the volatile compound into an infinite quantity of the polymeric stationary phase. An absolute value of the excess molar enthalpy, ΔH_m^{∞}, is derived from the temperature dependence of the activity coefficients. The results obtained using eq 8 and a linear regression on the data presented in Figure 2 (solid lines)

Table III. Molar Enthalpy of Mixing Ethylcellulose and Chlorinated Alkanes

			ΔH_m^∞ (kJ mol^{-1})[a] for given casting solvent[b]			
temp range (°C)	thermal history	probe	$CHCl_3$[c]	CH_3CCl_3[c]	CH_2Cl_2[c]	CH_2Cl_2[d]
50–90	no annealing	$CHCl_3$	−19.0 ± 0.7	−20.2 ± 0.4	−24.8 ± 1.7	−25.3 ± 2.2
		CH_3CCl_3	−14.9 ± 0.8	−16.7 ± 0.6	−21.6 ± 0.3	−21.7 ± 1.6
		CH_2Cl_2	−14.2 ± 0.8	−15.0 ± 0.4	−18.4 ± 0.7	−18.6 ± 1.6
50–90	annealed at 175 °C	$CHCl_3$	−25.8 ± 1.5	−23.0 ± 0.7	−25.9 ± 0.9	−26.8 ± 1.0
		CH_3CCl_3	−19.8 ± 0.6	−18.4 ± 1.4	−23.5 ± 0.6	−26.4 ± 1.5
		CH_2Cl_2	−18.6 ± 0.5	−17.4 ± 1.2	−20.6 ± 0.6	−22.7 ± 0.7
130–170	annealed at 175 °C	$CHCl_3$	−6.0 ± 0.6	−6.1 ± 1.5	−8.5 ± 1.7	
		CH_3CCl_3	+0.3 ± 0.4	−0.8 ± 1.8	0 ± 3	
		CH_2Cl_2	−5.3 ± 0.5	−5.1 ± 1.1	−6 ± 3	

[a] Calculations were performed on the data of Figure 2, using eq 10. The uncertainty was determined from the 95% confidence interval on the slope of the linear regression. [b] Stationary phases cast from different solvents were prepared successively in the same column as described in the Experimental Section. [c] Column I. [d] Column II. Most experimental parameters are different for columns I and II, including the chromatograph, the column length, and the polymer content.

are given in Table III. The uncertainty on ΔH_m^∞ was calculated from the 95% confidence interval on the slope. It is on the order of 2–5%, except above T_g, where the much smaller slope of the activity coefficient increases the confidence interval. The enthalpy of mixing obtained for the same system on two different chromatographic columns allows us to evaluate the effect of the polymer content. The comparison of the last two columns of Table III shows a remarkable agreement between the results. This is a clear indication that there is no effect of the thickness of the stationary phase, even below its glass transition. Therefore, there is no sizable contribution of surface adsorption to the retention of the probe, and the enthalpy calculated is only the thermal effect of forming the solution. Upon close examination of Table III, some trends can be noticed. Below T_g, the enthalpy of mixing is negative for all probes and stationary phases. However, ΔH_m^∞ measured from the retention above T_g is significantly larger (less negative) for mixtures of EC with 1,1,1-trichloroethane than with the other probes. In fact, solutions of EC in CH_3CCl_3 at high temperature appear to be essentially athermal. A possible explanation could be that, in contrast with chloroform and dichloromethane, 1,1,1-trichloroethane does not possess an acid hydrogen, therefore limiting hydrogen bonding to ether functions of EC. At low temperature, an identical trend is observed whatever the history of the stationary phase: the enthalpy of mixing is the largest upon mixing with dichloromethane and the smallest for solutions with chloroform. Although the value of ΔH_m^∞, as well as its change upon devitrification, depends on the probe, the effect is qualitatively the same for all solutions: mixing with the glassy polymer brings about a larger loss in the enthalpy of the system than mixing with the polymeric liquid. The magnitude of the drop depends on the probe, varying from 12 to 23 kJ mol^{-1}. These are high values, in fact on the order of magnitude of half the enthalpy of vaporization of the pure probe. Such large negative contributions to mixing functions are reminiscent of the general phenomenon which has been shown[33,34] to occur upon mixing two nonpolar liquids having very different molecular sizes, e.g., an amorphous polymer above T_g and a solvent. In the presence of the polymeric liquid, the more expanded solvent contracts. This decrease in the solvent free volume brings a negative contribution to the heat of mixing. This effect is at least partly responsible for the negative enthalpies of mixing of EC and chlorinated alkanes above T_g. The large decrease in ΔH_m^∞, observed when mixing is performed below T_g rather than at high temperature, indicates that the solvent experiences a large loss of mobility in the glassy matrix. This reduces the enthalpy of the solution, since it contributes to improve the polymer–solvent contacts.

Conclusions

The properties of EC and its highly concentrated solutions with various chlorinated probes have been studied by IGC, using the first moment of the elution profile to measure retention parameters independent of flow rate. Due to the existence of chiral nematic phases in solution, EC forms an orientationally ordered glass upon casting at room temperature. When heated, the cast film experiences a glass transition at a temperature which depends on the casting solvent and the thermal history of the sample. Annealing above T_g induces some recrystallization and improves the overall orientation in the film but does not completely erase the solvent history. The effect is attributed to differences in the liquid crystalline structure of the films. The excess enthalpy of mixing, calculated from the temperature dependence of the activity coefficients of the probe, is a sensitive indicator of the physical state of the stationary phase. For given probe and stationary phases, the enthalpy of mixing is much lower for the glass than for the corresponding liquid above T_g. Also, ΔH_m^∞ calculated below T_g for a given probe is lower after annealing the stationary phase. The results indicate that the thermodynamics of mixing mainly reflect the change experienced by the probe upon dissolving into a glass: the considerable loss of mobility improves the contacts with the polymeric matrix, therefore reducing the enthalpy of the system. In the present study, equilibrium retention parameters were obtained by IGC at temperatures much lower than T_g. This is due in part to the use of moment analysis but also to a lower resistance to mass transfer in EC than in an ordinary amorphous glass. Further insight into the structural properties of orientationally ordered glasses can be gained from the study of the diffusion of the volatile compound in the polymer. This is the subject of a following paper[35] reporting the diffusion coefficients calculated from the second moment of the elution profiles of chloroform, dichloromethane, and 1,1,1-trichloroethane on the various EC stationary phases.

Acknowledgment. Financial support from the Natural Sciences and Engineering Council of Canada is gratefully acknowledged. J.-Y.W. is grateful to the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (Province of Québec) for a scholarship. Thanks are also due to Dr. C. Bhattacharya for performing the heat capacity measurements.

References and Notes

(1) Wang, J.-Y.; Charlet, G. *Macromolecules* **1989**, *22*, 3781.

(2) Braun, J. M.; Guillet, J. E. *Adv. Polym. Sci.* **1976**, *21*, 107.

(3) Gray, D. G. *Prog. Polym. Sci.* **1977**, *5*, 1.

(4) Laub, R. J.; Pecsok, R. L. *Physicochemical Applications of Gas Chromatography*; Wiley: New York, 1980.

(5) Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley: New York, 1979.

(6) Vîlcu, R.; Leca, M. *Polymer Thermodynamics by Gas Chromatography* (*Studies in Polymer Science 4*); Elsevier: New York, 1990.

(7) Munk, P.; Hattam, P.; Du, Q.; Abdel-Azim, A. A. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1990**, *45*, 289.

(8) Munk, P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32*, 515.

(9) Orts, W. J.; Romansky, M.; Guillet, J. E. *Macromolecules* **1992**, *25*, 949.

(10) Du, Q.; Hattam, P.; Munk, P. *J. Chem. Eng. Data* **1990**, *35*, 367.

(11) Mandal, B. M.; Bhattacharya, C.; Bhattacharya, S. N. *J. Macromol. Sci., Chem.* **1989**, *A26*, 175.

(12) Munk, P.; Hattam, P.; Abdel-Azim, A. A.; Du, Q. *Makromol. Chem., Macromol. Symp.* **1990**, *38*, 205.

(13) Demertzis, P. G.; Riganakos, K. A.; Akrida-Demerti, K. *Eur. Polym. J.* **1991**, *27*, 231.

(14) Hattam, P.; Munk, P. *Macromolecules* **1988**, *21*, 2083.

(15) Wang, J.-Y. Ph.D. Thesis, Laval University, 1992.

(16) Gray, D. G. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 257.

(17) Harkness, B. R.; Gray, D. G. In *Liquid Crystalline and Mesomorphic Polymers*; Shibaev, V., Lam, L., Eds.; Springer-Verlag: New York, 1991.

(18) Suto, S.; Oikawa, K.; Karasawa, M. *Polym. Commun.* **1986**, *27*, 262.

(19) Budgell, D. R. Ph.D. Thesis, McGill University, 1990 (*Diss. Abstr. Int. B* **1991**, *51* (9), 4371).

(20) Guo, J.-X.; Gray, D. G. *Macromolecules* **1989**, *22*, 2082.

(21) Martire, D. E. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R., Gray, G. W., Eds.; Academic Press: London, 1979.

(22) Patterson, D.; Tewari, Y. B.; Schreiber, H. P.; Guillet, J. E. *Macromolecules* **1971**, *4*, 356.

(23) Guillet, J. E.; Romansky, M.; Price, G. J.; van der Mark, R. In *Inverse Gas Chromatography*; Douglas, R., Lloyd, T., Ward, C., Schreiber, H. P., Pizaña, C. C., Eds.; ACS Symposium Series 391; American Chemical Society: Washington, DC, 1989; p 20.

(24) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.

(25) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(26) Compare, for instance, Figure 1 with the results obtained on amorphous polystyrene (Figure 4 in ref 1).

(27) Wunderlich, B.; Grebowicz, J. *Adv. Polym. Sci.* **1984**, *60/61*, 1.

(28) Suto, S.; White, J. L.; Fellers, J. F. *Rheol. Acta* **1982**, *21*, 62.

(29) Meesiri, W.; Menczel, J.; Gaur, U.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 719.

(30) An exotherm is also observed upon heating the as-received powder.

(31) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.

(32) Menczel, J.; Wunderlich, B. *Polymer* **1981**, *22*, 778.

(33) Patterson, D.; Delmas, G.; Somcynski, T. *Polymer* **1967**, *8*, 503.

(34) Patterson, D. *J. Polym. Sci., C* **1968**, *16*, 3379.

(35) Wang, J.-Y.; Charlet, G., to be published.