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Polymer Conformation and Viscometric Behaviour

1. Conformational Transition in Poly (Benzyl Methacrylate) in Dilute Solutions

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Summary

The viscometric and refractometric behaviour of poly (benzyl methacrylate) (PBM) in isobutyl methyl ketone (IMK) as a function of the temperature was studied. The viscometric relations in IMK and toluene by membrane osmometry and GPC at 25°C were established. The viscometric results show discontinuities in the intrinsic viscosity $[\eta]$ in IMK and sharp changes in the conformational and thermodynamic parameters K_θ and B. The variation on the unperturbed dimensions of the polymer chain was attributed to a conformational transition. The influence of the side groups was analyzed. The conformational behaviour of this polymer was compared with the saturated corresponding poly (cyclohexyl methyl methacrylate).

Introduction

Conformational transitions of various poly(methacrylic ester)s have been investigated by several authors (KATIME, et al., 1974; SARABIA, et al., 1981; DONDOS, et al., 1973). It has been recently found that poly(cyclohexyl methacrylate), (poly[1-(cyclohexyloxycarbonyl)-1-methylethylene]) (PCM) and poly(cyclohexyl methyl methacrylate) (poly[1-(cyclohexylmethoxycarbonyl)-1-methylethylene]) (PCMM) can undergo a conformational transition in isobutyl methyl ketone (IMK) (KATIME, et al., 1981; GARGALLO, et al., 1983). The phenomenon has been characterized by a discontinuity of the unperturbed dimensions of the polymer. It seems that the side groups play an important rol in this phenomenon as it has been pointed out (KATIME, et al., 1981; GARGALLO, et al., 1983). If the side group is the main responsable of the conformational transition of the polymer, we would expect that the nature of the transition would be different when the same polymer backbone have different pendant groups, as it would be the case of polymethacrylates with aromatic or alicyclic side groups.

The purpose of this study is to obtain information on the conformational transition induced by temperature in poly (benzyl methacrylate) (poly[1-benzyloxycarbonyl)-1-methylethylene) (PBM) in the same solvent and to compare the behaviour of this polymer with that of PCMM.

In order to study this effect we have prepared poly (benzyl methacrylate) and we have investigated the viscometric behaviour in IMK solutions as a function of the temperature. The polymer was previously characterized by osmometric, viscometric and gel permeation chromatography (GPC) measurements.

Experimental

Monomer and Polymer Preparation

The monomer benzyl methacrylate was prepared by reaction of methacryloyl chloride (0.15 mol) with benzyl alcohol (0.12 mol) in benzene solution and N,N-dimethylaniline (0.12 mol) at reflux temperature during 32 h. according with the technique described by BURTLE, et al., (1954). Purification was achieved by distillation under vacuum. B.p. (1 mm Hg) 121°C, yield 85%.

Benzyl methacrylate was polymerized at 50% in benzene solutions under vacuum in sealed glass tubes, in presence of 2,2'azoisoburonitrile (AIBN), $5 \cdot 10^{-4}$-$2 \cdot 10^{-2}$% (w/w).

The polymer was fractionated by solubility in benzene/methanol. Nine fractions were obtained.

The number-average molecular weights, $\bar{M}_n$, were determined by osmometry in toluene at 25°C with a Hewlett - Packard high-speed membrane osmometer, model 502. The measurement were usually made at four or five different concentrations and extrapolated to infinite dilution.

The weight-average molecular weights $\bar{M}_w$, were determined by gel permeation chromatography (GPC) with a Perkin-Elmer High Performance Liquid Chromatograph (HPLC) equipped with a 6000-psi pump, a Perkin-Elmer differential refractometer LC-25, a injector of 175 μl, and Shodex A805/S column (molecular weight, range 10^4-$5 \cdot 10^6$). Samples were eluted with tetrahydrofuran (THF). The apparatus was calibrated with fractions of polystyrene with narrow molecular weight distribution characterized by light scattering and membrane osmometry. The flow rate was 1 ml/min and the volume of the injected polymer solution was always 5 μl.

The viscosities of poly(benzyl methacrylate) fractions in toluene at 25°C and IMK at different temperatures were measured with a DESREUX-BISCHOFF, (1950) dilution viscometer and the intrinsic viscosity $[\eta]$ was determined by the usual extrapolation of the reduced specific viscosity η_{sp}/c and $(\ln \eta_r)/c$ versus c; (η_r= relative viscosity).

The refractive index increments of the polymer solution in IMK were measured at different temperatures using a Brice-Phoenix Differential Refractometer, BP 2000. Aqueous solutions of purified KCl at 298 K were used for the calibration of the differential refractometer.

Results

Six fractions of the polymer were selected for the present physical chemical measurements from a number of nine final fractions.

The osmometric measurement show a regular behaviour and the plots of the reduced osmotic pressure π/c versus concentration c (Fig. 1) agree with classical relations (KRIGBAUM, et al., 1952; FOX Jr., et al., 1951).

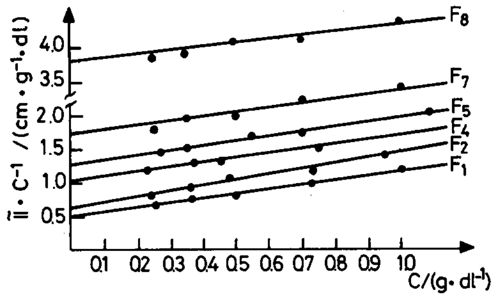

Figure 1. Variation of the reduced osmotic pressure π/c, (π in cm of solvent, c in $g \cdot dl^{-1}$) with the concentration c for six poly(benzyl methacrylate) fractions in toluene solutions at 25°C.

The variation of A_2 with the molecular weight shows also a regular behaviour (BERRY, et al., 1970) and the following empirical relation was found. $A_2 = 2.4 \cdot 10^{-5} \bar{M}_n^{-0.17}$ which agrees with a linear flexible polymer.

Table 1 summarizes the molecular and viscometric characterization of the fraction i.e. weight average molecular weight, number average molecular weight, molecular weight distribution, second virial coefficient A_2, and intrinsic viscosity $[\eta]$ data in toluene and IMK at 25°C.

Kuhn-Mark-Houwink relations at 25°C were established in toluene and IMK by plotting the intrinsic viscosity against number-average molecular weight $\bar{M}_n$ and weight average molecular weight, $\bar{M}_w$. The experimental data show that poly(benzyl methacrylate) depends on the quality of the solvent. The following empirical relations were obtained.

Table 1. Molecular characterization of poly(benzyl methacrylate) fractions.

Fraction	$(\pi/c)_{c=0}$	$\bar{M}_n$ x 10^{-5} a)	A_2 x 10^4 (cc mol g^{-2})	$\bar{M}_w$ x 10^{-5} b)	$[\eta]/(dl\ g^{-1})$ 25°C toluene	$[\eta]/(dl\ g^{-1})$ 25°C IMK	$I = \bar{M}_w/\bar{M}_n$ a) b)
F_1	0.52	5.59	2.39	5.96	0.616	0.455	1.07
F_2	0.63	4.62	2.30	5.01	0.558	0.370	1.08
F_3	—	—	—	4.73	0.495	0.328	—
F_4	1.05	2.77	2.30	3.60	0.438	0.305	1.30
F_5	1.29	2.25	2.40	2.66	0.339	0.266	1.18
F_6	—	—	—	2.37	0.313	0.235	—
F_7	1.76	1.65	2.60	1.68	0.240	0.187	1.03
F_8	3.75	0.77	2.90	0.84	0.142	0.120	1.09

a) From membrane osmometry; b) From GPC.

$$[\eta] = 3.6 \times 10^{-5}\ \bar{M}_n^{0.74} \quad \text{(toluene 25°C)}$$
$$[\eta] = 10.1 \times 10^{-5}\ \bar{M}_n^{0.63} \quad \text{(IMK 25°C)}$$
$$[\eta] = 3.0 \times 10^{-5}\ \bar{M}_w^{0.75} \quad \text{(toluene 25°C)}$$
$$[\eta] = 9.0 \times 10^{-5}\ \bar{M}_w^{0.64} \quad \text{(IMK 25°C)}$$

Fig. 2 shows the variation of intrinsic viscosity $[\eta]$ in isobutyl methyl ketone with the temperature between 5 to 30°C.

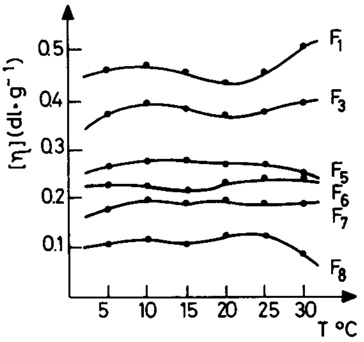

Figure 2. Variation of the intrinsic viscosity $[\eta]$ with the temperature for six fractions of poly(benzyl methacrylate) in isobutyl methyl ketone.

Discussion

The viscometric behaviour of the polymer fraction shows discontinuities in the intrinsic viscosity $[\eta]$ as a function of the temperature. This type of behaviour has been interpreted as a conformational change of the polymer chain (KATIME, et al., 1974, 1977, 1981). The qualitative viscometric behaviour is similar to that of poly(cyclohexyl methyl methacrylate)(GARGALLO, et al., 1983).

It is necessary to know if the behaviour shown through viscometric measurements is refleted in the unperturbed dimensions of the polymer chain.

In order to separate both types of interaction involved in $[\eta]$, we have used one of the excluded volume theories to determine if the experimental viscometric behaviour is of intra or intermolecular nature. Therefore, in order to find the value of the conformational parameter K_θ, leading to the unperturbed dimensions $\langle r^2_0\rangle^{1/2}$ given by: $K_\theta = \Phi_0(\langle r^2_0\rangle/M)^{3/2} = [\eta]_\theta/M^{1/2}$, the STOCKMAYER-FIXMAN (1963) equation was employed.

The Stockmayer-Fixman plots show differents extrapolations intercepts for different temperatures. This is indicative of different unperturbed states. Fig. 3 shows the variation of the unperturbed dimensions parameter K_θ and the thermodynamic parameter B (also obtained from the Stockmayer-Fixman plot) as a function of the temperature. Poly(benzyl methacrylate) exhibits considerable changes in K_θ and B in the temperature range between 5 to 30°C.

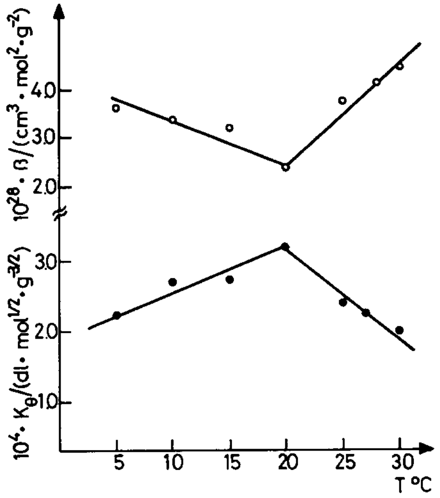

Figure 3. Variation with temperature of conformational parameter K_θ and thermodynamic parameter B from Stockmayer-Fixman plot of poly(benzyl methacrylate) in isobutyl methyl ketone.

As can be seen in Fig. 3. K_θ shows a maximum at 20°C and the thermodynamic parameter B shows a minimum at the same temperature. From the change in K_θ it is possible to visualize the conformational change of the polymer change where the polymer goes from a flexible to a more rigid form when the temperature increase up to 20°C and then the chain reaches its original flexibility.

On the other hand, the variation of the molecular interaction thermodynamic parameter B shows a minimum at the transition temperature which would indicate that in the transition zone the number of polymer-solvent contacts decreases. This effect should be directly related to the partial specific volume of the polymer $\bar{v}$. Because dn/dc is directly related to $\bar{v}$, the refractive index increments measurements were determined, in order to estimate the variation of $\bar{v}$.

Fig. 4 shows the variation of dn/dc with the temperature which also confirms that polymer-solvent contacts decreases. This can be explained because the polymer-polymer contacts are favoured. Effectively, the increase in the polymer rigidity can be explained assuming that as the temperature increase between 5 to 20°C there is a greater rotational freedom of the carbon atoms around the valence cone, but at the same time this rotational freedom favours the adequate geometry for the interaction between aromatic rings, with the consequent increase in the rigidity of the chain. At 20°C the conformational transition occurs and the rotational freedom is stil greater because of a bigger flexibility of the polymer chain.

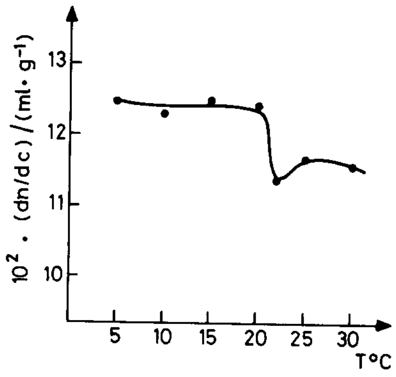

Figure 4. Variation of the refractive index increment dn/dc with the temperature for one poly(benzyl methacrylate) fraction in isobutyl methyl ketone.

The importance of the interaction among aromatic groups and the effect that this kind of interaction produces in the rigidity of the polymer chain has been widely discussed (HADJICHRISTIDIS, et al., 1972; BECERRA, et al., 1978). Therefore, when we compare from a conformational point of view an aromatic and alicyclic polymer we should expect a different behaviour, because of the different flexibility of the polymer chain which is another factor that plays an important rol in the conformational transition of the polymer chain.

The above seems ot indicate that there is specific interactions between side groups which are playing an important rol in the stabilization of a determined conformation of the polymer in solution avoiding some modifications when the temperature increases.

Let us compare the temperature transition range between poly(benzyl methacrylate) and that of poly(cyclohexylmethyl methacrylate), which is the corresponding saturated homologous. We can see that there is a shift to higher temperatures values in the case of poly(benzyl methacrylate). This behaviour could be explained as a consequence of the rigidity of the aromatic polymer which would be another argument to think that the main factor in the conformational behaviour of poly(methacrylic ester)s is the influence of the nature of side groups.

In order to clarify this behaviour in several polymer-systems and to give a general explanation we are at present working with other polymers and copolymers with benzyl and cyclohexyl groups in the side chain.

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