sonable consequence since the compartmentalization of paired anthroate groups will not be as rigid as in the PAEU polymers.

Now the differentiation between rotational and swinging motions of terminal groups is possible. The former is allowed for polyesters but not for polyester urethanes at −196 °C. The latter, which is responsible for remaking dianthracene units from unpaired anthroate groups, is released well below T_g for polyesters but not for polyester urethanes. Although the present information is qualitative, the good parallelism among all pieces of information on various terminal segment mobilities would be a manifestation that the freedom of various mobilities is governed by the same structural factors.

Conclusion

We observed directly the mobility of terminal anthroate groups in polyesters and polyester urethanes. The finding that the terminal group mobility is not related to T_g is worth being emphasized. Very small mobilities are responsible for characteristic photochemical and photophysical properties of terminal groups, which are most strongly affected by inter- or intrapolymer hydrogen bonding.

The information on structural factors influencing terminal and pendant segment mobilities will be useful in the molecular engineering of photoresponsive polymers, although the present polymers themselves will have no practical values due to poor reversibility of photochromism.

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Conformational Characteristics of Poly(methyl acrylate). 1. Dipole Moment Measurements

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ABSTRACT: A sample of poly(methyl acrylate) with $M_v = 4.57 \times 10^5$ has been synthesized via free-radical polymerization. Six fractions having molecular weights $M_v = 4.70 \times 10^5$, 10.12×10^5, 6.90×10^5, 4.99×10^5, 4.49×10^5, and 3.33×10^5 were isolated, and their dipole moments in benzene solution were determined at different temperatures in order to study the effect of molecular weight and temperature on the dipole moment. The plot of dipole moment ratio against temperature exhibits a minimum at $T \simeq 35$ °C that, to our knowledge, has not been reported before; however, this ratio does not depend on molecular weight.

The published data concerning experimental dipole moment measurements of poly(methyl acrylate) (PMA) in solution are scarce;[1-3] the dependence of dipole moment on temperature has not yet been investigated. The aim of the present paper is to elucidate the dependence of PMA dipole moment on temperature from an experimental point of view in order to expand the knowledge on this topic. The experimental values of dipole moment will help, with an adequate theoretical interpretation, us to a better understanding of the conformation of PMA in solution. Our results show that the variation of dipole moment with temperature exhibits a transition, similar to the one found for some other polymers,[4,5] that indicates a change in short-range interactions at a given temperature.

For the present work, a sample of PMA has been synthesized, fractionated, and characterized (both the raw sample and the fractions) by viscometry. The dipole moment, evaluated according to the method of Guggenheim and Smith,[6,7] has been determined as a function of temperature and of molecular weight.

Experimental Section

(a) Materials. The monomer (methyl acrylate, Fluka, pure) was distilled under reduced pressure just before utilization in order

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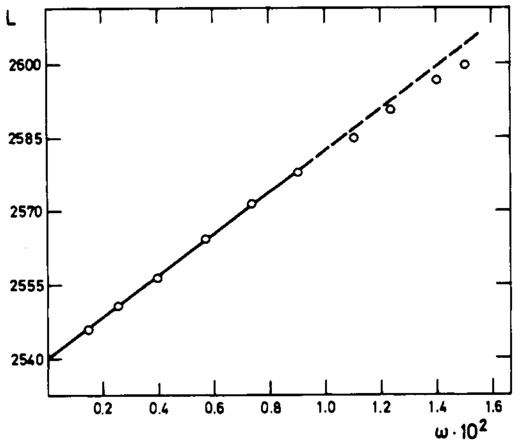

Figure 1. Dependence of L (dielectric constant in arbitrary units) on ω (weight fraction of polymer in the solution) for unfractionated PMA in benzene solution at 25 °C.

to eliminate the stabilizer. Toluene, used as solvent (Riedel-Häen, chromatografic quality (99.9% purity)), was distilled over sodium wire. Polymerization[1,8,9] was carried out at 70 °C, using benzoyl peroxide as initiator. Initial concentrations of monomer and initiator were 5×10^{-3} and 8×10^{-7} M, respectively; the time allowed for reaction was 30 min. The polymer obtained was precipitated by pouring the reaction mixture on methanol. This gave a rubber-like sample which was difficult to manipulate. It was redissolved in benzene and precipitated again by pouring it into boiling water;[9] the sample thus obtained was more compact and easy to manipulate; this sample was dried under reduced pressure at room temperature.

The molecular weight of the polymer was determined by viscometry in benzene at 25 °C. The viscosity equation used was[10]

$$|\eta| \text{ (dL/g)} = 1.282 \times 10^{-4} M^{0.7143} \tag{1}$$

and the molecular weight found $M_v = 4.57 \times 10^5$.

(b) Fractionation. The raw sample was dissolved in benzene and fractionated by addition of methanol as precipitant. Each one of the collected fractions was redissolved in benzene, precipitate on boiling water, and dried as explained above; its molecular weight was evaluated also by viscometry. Two different fractionations were carried out: the first one was intended to give fractions large enough to measure the dipole moments as a function of temperature; the second one was aimed at obtaining several samples with different molecular weights in order to study the dependence of dipole moment on molecular weight.

Six samples were selected for the present work; they will be called PMA1B, PMA2A, PMA2B, PMA2C, PMA2D, and PMA2E (the first one comes from the first fractionation and the remaining five come from the second fractionation); their viscosity average molecular weights are 4.70×10^5, 10.12×10^5, 6.90×10^5, 4.99×10^5, 4.49×10^5, and 3.33×10^5, respectively.

(c) Dielectric Measurements. All dielectric measurements were performed on a WTW Model DK-06 dipolmeter at a frequency of 6.2 MHz. The cell used was made of silvered Pyrex glass, and the measured solutions acted as the dielectric of a capacitor. The cell was calibrated at every working temperature, using compounds with well-known dielectric constants[11,12] (i.e., benzene, toluene, and cyclohexane). All the substances used for calibration were pure and freshly distilled over sodium wire. The variation of the calibration constant K with temperature was negligible, within the range of working temperatures; its value for 25 °C will be used henceforth.

Some preliminary measurements were carried out with the raw polymer at 25 °C in order to determine the best range of concentrations. The dependence of dielectric constant (in arbitrary units, L) on the weight fraction of polymer, ω, is shown in Figure 1. As can be seen, this dependence is not linear beyond $\omega \simeq 0.8 \times 10^{-2}$; all measurements have been made for concentrations smaller than this value.

Several benzene solutions of each fraction with concentrations ranging from $\omega \simeq 0.001$–0.008 were prepared by dilution of concentrated solutions.

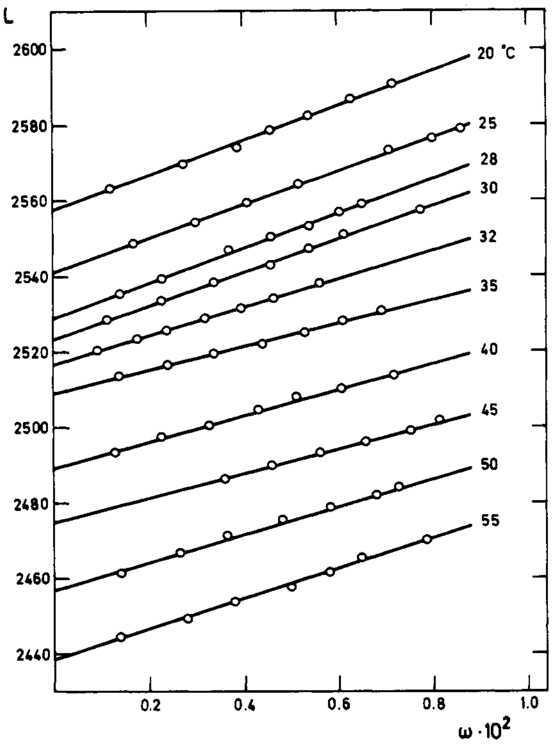

Figure 2. Dependence of L on ω for fraction PMA1B in benzene solution at the temperatures indicated. (See legend for Figure 1.)

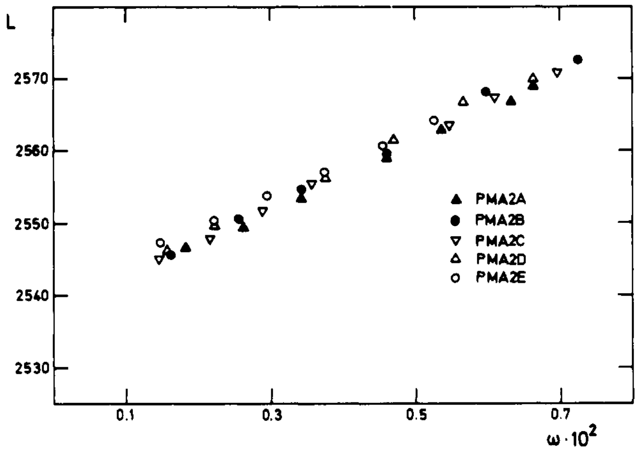

Figure 3. Dependence of L on ω for the fractions PMA2A, PMA2B, PMA2C, PMA2D, and PMA2E in benzene solution at 25 °C. (See legend for Figure 1.)

The dielectric constant of PMA1B solutions was measured at several temperatures ranging from 20–55 °C; the temperature regulation is ±0.05 °C. The solutions of the remaining five fractions (PMA2A to PMA2E) were measured at 25 ± 0.05 °C. The results (in arbitrary units, L) are summarized in Figures 2 and 3.

(d) Refractive Indices. The differences between the refractive index of solutions and pure solvent, Δn, were measured on a Brice-Phoenix Model 2000-V differential refractometer at wavelengths of $\lambda = 546$ and 436 nm. The range of concentrations was the same as that for dielectric measurements. The refractive index of pure solvent was measured on a Bausch and Lomb Model 33-45-02-01 refractometer at $\lambda = 589$ nm.

Results

Values of the mean-square dipole moment $\langle\mu^2\rangle$ were calculated from the following equation of Guggenheim and Smith:[6,7]

$$\langle\mu^2\rangle = \frac{27kTM}{4\pi N(\epsilon_1 + 2)^2 d_1}\left[\left(\frac{d\epsilon}{d\omega}\right)_{\omega\to 0} - \left(\frac{dn^2}{d\omega}\right)_{\omega\to 0}\right] \tag{2}$$

Table I
Values of $(d\epsilon/d\omega)_{\omega\to 0}$ for Fraction PMA1B at Different Temperatures

T, °C	20.00	25.00	28.00	30.00	32.00	35.00	40.00	45.00	50.00	55.00
$(d\epsilon/d\omega)_{\omega\to 0}$	2.87	2.72	2.80	2.79	2.26	1.90	2.09	2.04	2.35	2.53

Table II
Values of $(d\epsilon/d\omega)_{\omega\to 0}$ for PMA-Benzene Solutions at 25 °C

fraction	PMA2A	PMA2B	PMA2C	PMA2D	PMA2E
$(d\epsilon/d\omega)_{\omega\to 0}$	2.85	2.97	2.93	2.97	2.82

where k is the Boltzmann constant, N is the Avogadro number, T is the absolute temperature, d_1 is the solvent density, ϵ and ϵ_1 are the dielectric constants of solution and of pure solvent, respectively, ω is the solute weight fraction, and n is the solution refractive index. The molecular weight of the repeat unit is used as the M value, and therefore the dipole moment obtained is per repeat unit: $\mu_{\mathrm{eff}} = \langle\mu^2\rangle/x$.

In Figures 2 and 3, the measured dielectric constants (in arbitrary units, L) are plotted against the weight fraction ω of polymer in the solution. The values $(dL/d\omega)_{\omega\to 0}$ were obtained by the least-squares linear fit; the magnitude $(dL/d\omega)_{\omega\to 0}$ was transformed into dielectric constant units by using the cell calibration constant K. Table I shows the values of $(d\epsilon/d\omega)_{\omega\to 0}$ for fraction PMA1B at all measured temperatures, and Table II shows the values for the remaining five fractions at 25 °C.

The magnitude $(d\Delta n/d\omega)_{\omega\to 0}$ for fraction PMA1B was computed by the least-squares linear fit of the Δn values measured on its benzene solutions at 25 °C; the results were -1.3×10^{-2} and -7.5×10^{-3} at $\lambda = 436$ and 546 nm, respectively. These values were extrapolated according to Cauchy's method, giving the result -5.0×10^{-3} at $\lambda = 589$ nm; with this value and the measured refractive index of the pure solvent at the same wavelength and temperature ($n_1 = 1.49735$), a value of -1.5×10^{-2} was obtained for the magnitude $(dn^2/d\omega)_{\omega\to 0}$. This same value was used for computation of μ_{eff} in all cases (PMA1B at several temperatures and the remaining five fractions at 2.5 °C), since its incidence in the calculated μ_{eff} values is negligible.

Values of μ_{eff} computed according to eq 2 were reduced to the dimensionless dipole moment ratio $D_x = \mu_{\mathrm{eff}}/\mu_0^2$. The value $\mu = 1.76$ D, reported by Le Fevre et al.[1] for methyl propionate in benzene solution at 25 °C, was used as the dipole moment μ_0 of the repeating unit. Figure 4 shows the values of D_x as a function of x for the PMA2A, PMA2B, PMA2C, PMA2D, and PMA2E fractions; as can be seen from this figure, the ratio D_x does not depend on x and can be taken as its limiting value D_∞. The results of D_∞ for fraction PMA1B are plotted against temperature in Figure 5. D_∞ increases slowly as the temperature goes from 20 to 30 °C, then it decreases until 35 °C, reaching a minimum at this temperature, and finally it increases again as the temperature rises further.

Discussion

The values of D_x are insensitive to x within the range of molecular weights studied in the present work; this result agrees with the one reported by Le Fevre et al.[1] and indicates that the excluded volume has a negligible effect on the dipole moment of the polymer.

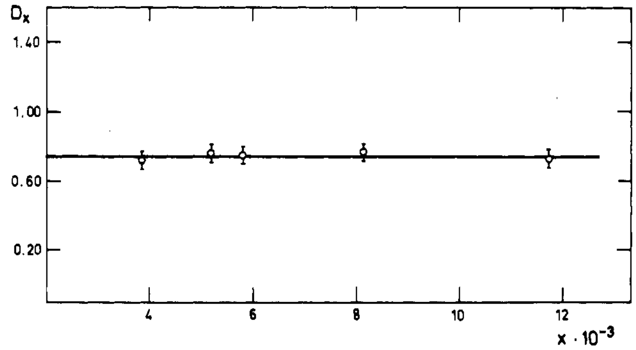

Figure 4. Dependence of D_x on the number of repeating units x for PMA in benzene solution at 25 °C.

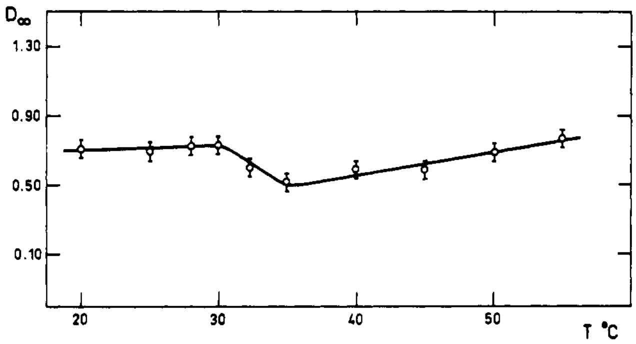

Figure 5. Dependence of D_∞ on temperature for fraction PMA1B in benzene solution.

To our knowledge, the only published experimental data about the variation of D_∞ with temperature are those of Kotera et al.,[3] who reported values at $T = 20$ and 50 °C, showing a slight increase of D_∞ (~5%) between these two temperatures. Our own results for the whole range between 20 and 55 °C indicate a slight overall decrease (~1%) from 20 to 50 °C that agrees within experimental error with Kotera's results. However, we find that D_∞ reaches a minimum at $T \simeq 35$ °C similar to the one found for isotactic poly(methyl methacrylate) in toluene solution[4] and poly(p-chlorostyrene) in toluene and isopropylbenzene solutions[5] but was never before reported for PMA. A possible explanation for this behavior could be a transition between two intramolecular states characterized by different short-range interactions; a suggestion about the nature of this transition in the PMA is presented in the following paper.[13]

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