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ADHESIVE POLYMER

INTERMACROMOLECULAR INTERACTION IN FLUID SOLUTION STUDIED BY FLUORESCENCE DEPOLARIZATION METHOD

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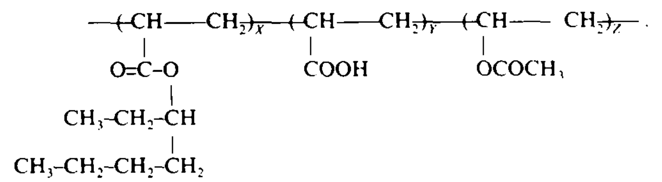
Abstract—The fluorescence depolarization of the anthryl groups attached to poly(styrene-maleic anhydride) [P(St-MA)] has been examined in mixtures of various acrylic adhesive polymers with toluene for weight fractions ranging from 0 to 0.25. It is clear that the relative mean rotational relaxation time of the anthryl groups sharply increases with increasing concentration of poly(2-ethylhexylacrylate) (PEHA) containing about 5% acrylic acid units and 10% vinyl acetate units. It may be concluded that an excellent adhesive polymer is made with acrylic acid units as agents for intra- and interaction and vinyl acetate units as depression agents for acrylic acid units and agents for strong PEHA P(St-MA) interaction.

INTRODUCTION

In previous communications from this laboratory, the concentration dependences of viscosities of acrylic polymers were measured to investigate the mechanism of adhesive phenomena of polymers [1]. The viscosity of poly(2-ethylhexylacrylate) containing about 8% acrylic acid units (PEHA0800) was smaller than that of homo-poly(2-ethylhexylacrylate) (PEHA0000) in dilute solution but the viscosity of PEHA0800 exceeded that of PEHA0000 in concentrated solution. This phenomenon could be attributed to intra- and inter-macromolecular hydrogen bonds between acrylic acid units of PEHA0800. On the other hand, the technique based on the labelled probe method has not been greatly used in the field of adhesive polymers. We showed that this technique is excellent for study of the dynamical behaviour of macromolecules in fluid solution [2–16]. It is essential that the properties of adhesive polymers should be examined in fluid solution because the solution property of an adhesive polymer is important to understand the dynamical chain motion of adhesive polymers.



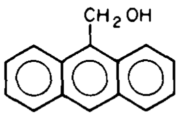
In this work, the fluorescence depolarization of the anthryl groups attached to poly(styrene-maleic anhydride) [P(St-MA)] was examined in mixtures of various acrylic adhesive polymers with toluene for weight fractions ranging from 0 to 0.25. The differences between the apparent mean rotational relaxation times of anthryl groups attached to P(St-MA) side-chain in various adhesive polymers is discussed briefly.

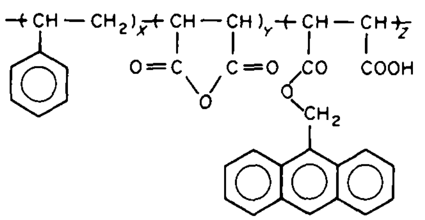
EXPERIMENTAL

Materials

Homo-poly(2-ethylhexylacrylate), (PEHA0000) and copoly(2-ethylhexylacrylate) containing acrylic acid and vinyl acetate units (PEHA0500, PEHA0510 and PEHA0800) were prepared using radical polymerization in a way similar to that used by many authors [1]. The number-average molecular weights and molecular-weight distributions of polymers were measured with a Toyo Soda HLC-802UR gel permeation chromatograph (GPC) at 40°C in THF. The viscosities of polymers were measured with an Ubbelohde viscometer at 25°C in toluene. Characteristics of adhesive polymer samples are PEHA0000 ($\bar{M}_n = 1.7 \times 10^5$, $\bar{M}_w/\bar{M}_n = 9.1$), PEHA0500 ($\bar{M}_n = 2.5 \times 10^5$, $\bar{M}_w/\bar{M}_n = 4.6$), PEHA0510 ($\bar{M}_n = 3.0 \times 10^5$, $\bar{M}_w/\bar{M}_n = 5.7$) and PEHA0800 ($\bar{M}_n = 4.1 \times 10^5$, $\bar{M}_w/\bar{M}_n = 5.6$), where $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of PEHA samples were calculated from $M_n^{PEHA} = ([\eta]^{PS}/[\eta]^{PEHA})M_n^{PS}$, superscript PS denoted polystyrene. In the notation for the adhesive polymer samples, the numbers after PEHA indicate the approximate percentage of acrylic acid units $[Y/(X + Y + Z) \times 100]$ and that of vinyl acetate units $[Z/(X + Y + Z) \times 100]$, for example, PEHA0510 is copoly(2-ethylhexylacrylate) containing 5% acrylic acid and 10% vinyl acetate units.

P(St-MA) was prepared using radical polymerization in a way similar to that used by many authors [13]. Anthryl groups were attached to the side-chain of P(St-MA) by reaction between the maleic anhydride units of P(St-MA) and 9-hydromethylanthracene (HMA). The P(St-MA) sample contained about 90% styryl and 10% maleic anhydride units. Characteristics of polymer samples are P(St-MA) ($\bar{M}_n = 1.3 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.5$) and P(St-MA)OA ($\bar{M}_n = 1.3 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.6$, content of anthryl groups = 2.7 per polymer molecule), where P(St-MA)OA signifies that the anthryl groups are attached to P(St-MA) side chain.





HMA (Aldrich Co.) was used as received. Dotite-Luminasol-grade toluene was used as solvent in measurement of fluorescence depolarization.

Measurements

The fluorescence depolarizations and spectra of P(St-MA)OA samples at concentrations between 10^{-6} and 10^{-5} (0.01–0.1 g/dl) were measured with Hitachi 650-40 type fluorescence spectrophotometer with polarizing filters (650-0155) [13].

RESULTS AND DISCUSSION

Concentration dependence of solution viscosity of acrylic adhesive polymer

The plots for η_{sp}/C vs concentration of PEHA in toluene at 25°C are linear for the range of about 0–0.1 g/ml. The intrinsic viscosity, $[\eta]$, is PEHA0000 (120 ml/g), PEHA0500 (45 ml/g), PEHA0510 (106 ml/g) and PEHA0800 (51 ml/g) [1]. PEHA0500 and PEHA0800 considerably shrink compared with PEHA0000 in a non-polar solvent. This effect can be ascribed to the intramacromolecular hydrogen bonds between acrylic acid units. On the other hand, the vinyl acetate units depress the intramacromolecular hydrogen bond between acrylic acid units. Consequently, PEHA0510 does not shrink in a non-polar solvent.

The plots for η_{sp} vs weight fraction of PEHA between 0 and 1.5% and between 0 and 25% are shown in Figs 1 and 2 respectively. In Fig. 1 for the range 0–1.5% PEHA, PEHA samples in which the content of acrylic acid units was varied showed the following increasing order of solution viscosity in toluene.

$$\text{PEHA0510} > \text{PEHA0000} > \text{PEHA0800} = \text{PEHA0500}.$$

The increasing ratio of solution viscosity of PEHA for the range 0–25% PEHA is summarized thus.

$$\text{PEHA0800} \gg \text{PEHA0500} > \text{PEHA0000} = \text{PEHA0510}.$$

These results show that the solution viscosity of PEHA has the following characteristics. The behaviour of solution viscosity of PEHA with more than 8% acrylic acid units is abnormal. It is suggested that this effect can be ascribed to intermacromolecular hydrogen bonds between acrylic acid units and that the vinyl acetate units depress the intermacromolecular interaction [1].

Measurement of fluorescence depolarization of rhodamine 6G in PEHA-toluene mixtures

The mean rotational relaxation time ρ related to the emission anisotropy r was calculated in a way similar to that reported previously [10–14]. The emission anisotropy can be calculated from

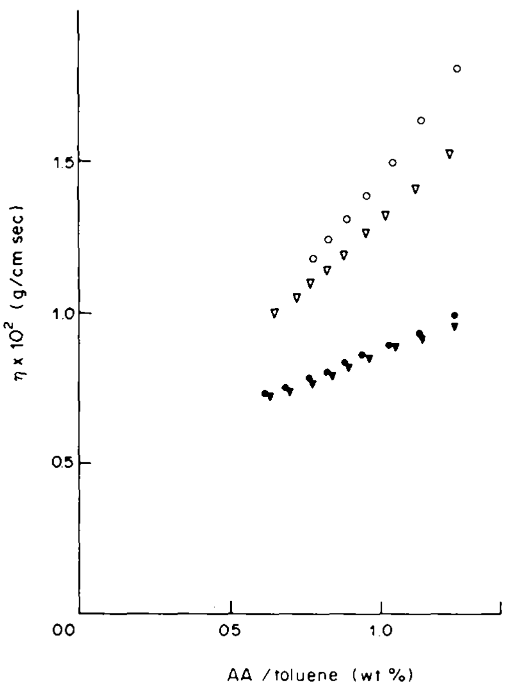


Fig. 1. Dependence of solution viscosity on weight fraction (%) of PEHA in toluene at 25°. (▽) PEHA0000; (▼) PEHA0500; (○) PEHA0510; (●) PEHA0800.

$$r = (I_{vv} - GI_{vh})/(I_{vv} + 2GI_{vh}) \tag{1}$$

where I is the intensity of emitted light, subscripts v and h denoting vertically and horizontally polarized light. The first suffix corresponds to the incident light, and second to the emitted light. The $G(= I_{hv}/I_{hh})$ factor in equation (1) is necessary to correct for the depolarization characteristics of the apparatus. The emission anisotropy is related to the mean rotational relaxation time ρ by

$$r_0/r = 1 + (3\tau/\rho) = 1 + (\mathrm{k}\tau/V)(T/\eta) \tag{2}$$

where τ is the excited singlet lifetime of the chromophore and r_0 is the emission anisotropy in rigid solution, and k and T are the Boltzman constant and the absolute temperature. As the ratio I_f/I_f^0 is proportional to τ/τ_0 by the relationship of $I_f \propto \mathrm{k}\tau$, where the subscript and superscript 0 represent the standard (in toluene), the ratio ρ/τ_0 for various mixed solvents can be expressed by

$$\rho/\tau_0 = 3I_f r_0^{-1}/I_f^0(r^{-1} - r_0^{-1}) \tag{3}$$

where I_f and I_f^0 are the fluorescence intensities at various PEHA concentrations and 0% PEHA, respectively. Consequently, the change of chromophore

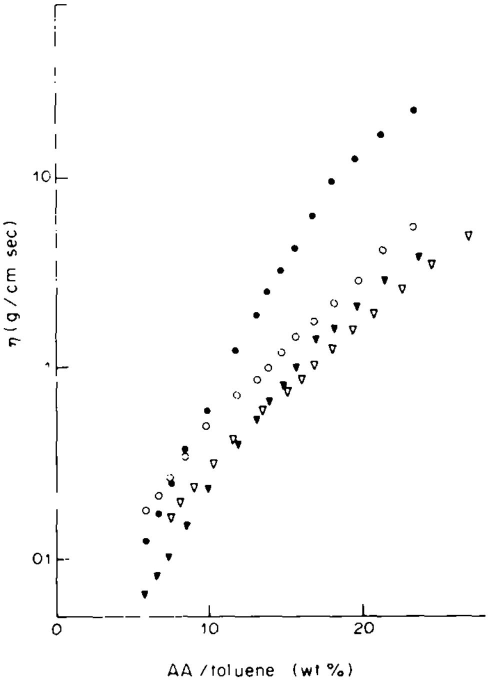


Fig. 2. Dependence of solution viscosity on weight fraction (%) of PEHA in toluene at 25°C. (▽) PEHA0000; (▼) PEHA0500; (○) PEHA0510; (●) PEHA0800.

lifetime for various PEHA–toluene mixtures is omitted using the parameter (I_f/I_f^0) in equation (3).

To obtain the emission anisotropy r_0 of rhodamine 6G (Rh6G), in rigid solution, the emission anisotropy r was measured in glycerine–water mixture [10]; its value is 0.31. The plots for the relative mean rotational relaxation time ρ/τ_0 of Rh6G vs η/T of PEHA–toluene mixtures are shown in Fig. 3. From equations (2) and (3), the relative mean rotational relaxation time in each mixed solvent can be expressed by

$$\rho/\tau_0 = (3V/k\tau_0)(\eta/T). \tag{4}$$

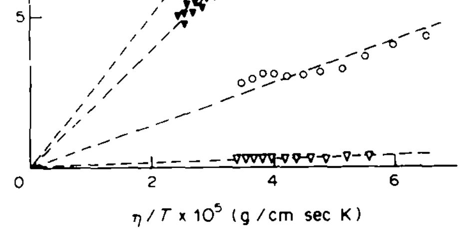


Fig. 3. Plots for relative mean rotational relaxation time of Rh6G against η/T for various PEHA–toluene mixtures. (▽) PEHA0000; (▼) PEHA0500; (○) PEHA0510; (●) PEHA0800.

In Fig. 3, the slopes show the apparent rotational volume $(3V/k\tau_0)$. These values are 7.5×10^3 cm/sec/K/g (PEHA0000), 2.0×10^5 cm/sec/K/g (PEHA0500), 7.0×10^4 cm/sec/K/g (PEHA0510) and 2.5×10^5 cm/sec/K/g (PEHA0800). Consequently, we can summarize the data referring to Rh6G and PEHA as follows, in order of the apparent rotational volume of Rh6G in various PEHA toluene mixtures.

PEHA0800 > PEHA0500
> PEHA0510 ≫ PEHA0000.

The phenomena can be ascribed to coulombic interaction between Rh6G and acrylic acid units of PEHA because Rh6G is a cationic chromophore. The change of apparent rotational volume of Rh6G in PEHA0000–toluene mixtures is suggested as based on a weak interaction between Rh6G and the ester groups of 2-ethylhexylacrylate units of PEHA. In Fig. 3, the increasing tendency of an apparent rotational volume of Rh6G with increasing content of acrylic acid units in PEHA corresponds to that of solution viscosity of PEHA for concentrated polymer solutions [1]. As is seen from the data for PEHA0510 in Fig. 3, the vinyl acetate units of PEHA depress the strong interaction (coulombic force) between Rh6G and acrylic acid unit.

Measurement of fluorescence depolarization of P(St-MA)OA in PEHA-toluene mixtures

To examine the adhesive polymer–polymer interaction, plots for the relative mean rotational relaxation time of P(St-MA)OA and HMA vs η/T of various PEHA–toluene mixtures are shown in Fig. 4. The increasing ratio of the apparent mean rotational

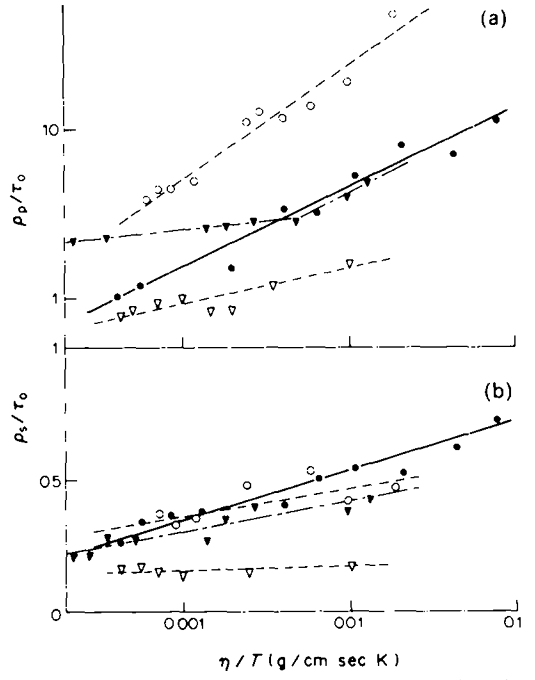


Fig. 4. Plots for relative mean rotational relaxation time of P(St-MA)OA and HMA against η/T for various PEHA–toluene mixtures. (a) P(St-MA)OA; (b) HMA. (▽) PEHA0000; (▼) PEHA0500; (○) PEHA0510; (●) PEHA0800.

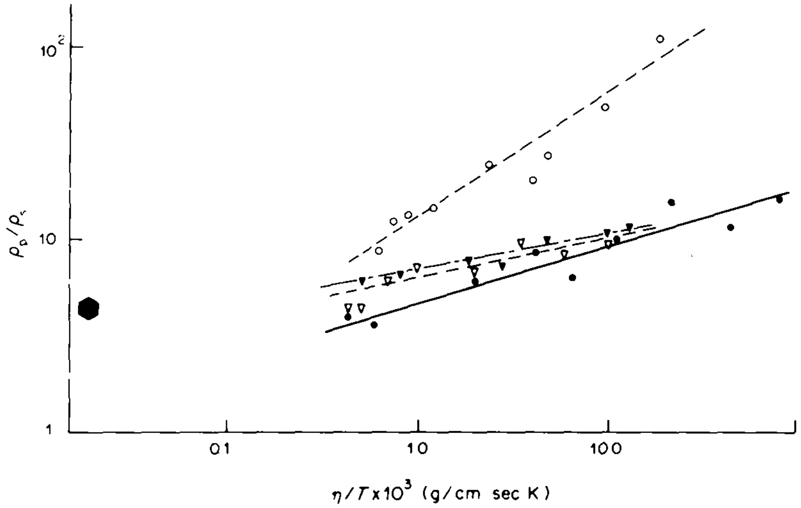


Fig. 5. Plots for ρ_p/ρ_s against η/T for various PEHA–toluene mixtures. (▽) PEHA0000; (▼) PEHA0500; (○) PEHA0510; (●) PEHA0800.

relaxation time of P(St-MA)OA is larger than that of HMA in Fig. 4. Consequently, it is suggested that the interaction between PEHA and P(St-MA)OA is stronger than that between adhesive polymer and HMA.

To facilitate an understanding of the adhesive polymer–polymer interaction, the ratio ρ_p/ρ_s in each mixed solvent can be calculated by,

$$\rho_p/\rho_s = \frac{[I_{fp} I^0_{fs} \tau_{0p} r_{0p}^{-1}(r_s^{-1} - r_{0s}^{-1})]}{[I^0_{fp} I_{fs} \tau_{0s} r_{0s}^{-1}(r_p^{-1} - r_{0p}^{-1})]} \qquad (5)$$

where p and s denote the chromophore attached to polymer chain [P(St-MA)OA] and small molecule (HMA), respectively. Equation (5) can be rewritten as follows by assuming $r_{0p} \cong r_{0s}$ and $\tau_{0p} \cong \tau_{0s}$,

$$\rho_p/\rho_s = \frac{(I_{fp} I^0_{fs}/I^0_{fp} I_{fs})[(r_s(r_{0s} - r_p)]}{[r_p(r_{0s} - r_s)]} \qquad (6)$$

where the r_0^{-1} value of HMA is 7.8 [13].

In order to clarify the interaction between adhesive polymer and polymer, a replot for $\log(\rho_p/\rho_s)$ vs $\log(\eta/T)$ is shown in Fig. 5. From equation (4), the ratio of apparent rotational volume (V_p/V_s), can be expressed by,

$$\rho_p/\rho_s = V_p/V_s. \qquad (7)$$

The increasing ratio of V_p/V_s in PEHA0510–toluene mixtures is larger than that in PEHA0000, PEHA0500 and PEHA0800–toluene mixtures. The result shows that PEHA0510 gives far stronger polymer–polymer interaction than any other PEHA sample in toluene. It can therefore be presumed that the strong interaction between polymers results from the use of vinyl acetate units in PEHA because PEHA0000, PEHA0500 and PEHA0800 do not contain vinyl acetate units. The vinyl acetate units in PEHA0510 make it a useful adhesive polymer.

CONCLUSION

In conclusion, the measurement of the emission anisotropy of anthryl groups chemically bound to the maleic anhydride units of P(St-MA) in PEHA–toluene mixtures shows that the ratio of V_p/V_s in PEHA0510–toluene mixtures increases to a much greater extent than any other mixtures. Our data show that various samples of PEHA have the following characteristics.

(a) Acrylic acid units in PEHA give rise to strong intra- and interaction (hydrogen bond) between PEHA molecules. Consequently, the radius of gyration of PEHA with acrylic acid units shrinks in dilute polymer solution, and the solution viscosity of PEHA with acrylic acid units increases with increasing concentration of polymer; the behaviour is abnormal for concentrated polymer solutions [1].

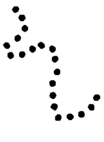
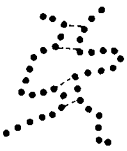
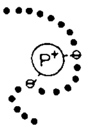
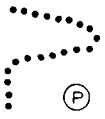
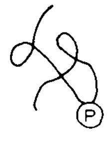
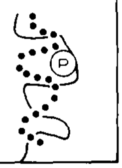
System	Interaction	Probe	Model
Adhesion -adhesion	Hydrogen bond		
Ionic chromophore -adhesion	Coulomb force		
Chromophore -adhesion	Viscosity increase		
Polymer -adhesion	Entanglement interpene-tration		

Fig. 6. Diagram of various interaction of PEHA in fluid solution.

(b) Acrylic acid units in PEHA give rise to coulombic interaction in non-polar solvent.

(c) Vinyl acetate units in PEHA make it an excellent adhesive polymer. The above-mentioned effect of acrylic acid units in PEHA is reduced by vinyl acetate units. Consequently, PEHA samples with both acrylic acid and vinyl acetate units have adequate intra- and interaction between PEHA molecules. The vinyl acetate units give rise to strong interaction between PEHA and general polymers.

(d) Consequently, it may be concluded that PEHA0510 (an excellent adhesive polymer) is made up of acrylic acid units as agents for intra- and interaction between PEHA0510 and of vinyl acetate units as a depression agent for the acrylic acid units and an agent for strong interaction between PEHA and general polymers.

The diagram for various interactions of PEHA in fluid solution is shown in Fig. 6. Since the present results are the first data on dynamical behaviour of an adhesive polymer in fluid solution, we are now trying to obtain data on dynamical behaviour of adhesive polymers in films to further support the previous [1] and present results. These data will be reported in the near future.

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