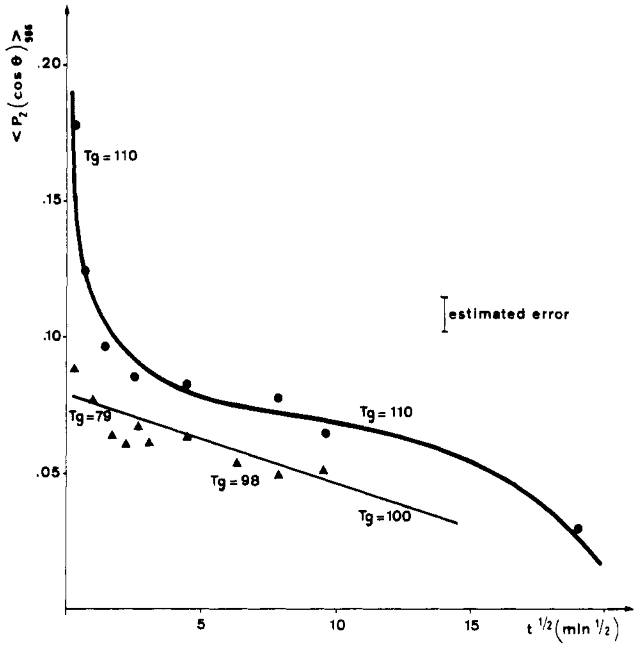

Figure 1. Orientation function and glass transition temperature as a function of time for polystyrene (▲, PS1; ●, PS2).

changing glass transition temperature, the determination of a relaxation time seems ambiguous.

If we now consider the PS2 data set in Figure 1, it is seen that this preparative technique effectively removes all solvent from the films since a constant T_g is observed. The PS2 data cannot be described by a single relaxation time. Hence, for this polystyrene at 115 °C and $\lambda = 4$, the MC model does not accurately describe the relaxation of orientation in this time range.

We now consider the second model, that of Doi and Edwards. In order to calculate the relaxation predicted by the DE model, several parameters must be known. The Rouse relaxation time τ_A has been shown to be 5.6 s for polystyrene at 120 °C.[6,7] We have shifted this value to our experimental temperature of 115 °C by the well-known WLF relation and obtained a value of $\tau_A(115\ °C) = 28$ s. Knowing τ_A, the other relaxation times have been calculated by scaling laws. The predicted values are $\tau_B = N^2\tau_A$ (since a limited number of Rouse subchains have to be considered, which modifies the numerical prefactor in the scaling law[7]) and $\tau_C = 3N\tau_B$, where N is the number of entanglements per chain. The value of N is obtained from the molecular weight between entanglements (18 000 for polystyrene).

The resulting predictions of the DE model are compared with the experimental data in Figure 2. The agreement with the model is quite reasonable. As already observed for other molecular weights, a slight divergence can still be noted at short times. Self-consistent corrections for the motions of the surrounding chains improve the agreement at long times.

Conclusions

Previous discrepancies in FTIR dichroism studies of chain relaxation are shown to arise from sample preparation artifacts, namely, plasticization of the melt by residual solvent. When measurements are made with consistently prepared samples, stretched close to the glass transition temperature, the relaxation of a high molecular weight polystyrene melt cannot be described by the reptation process alone. Additional relaxations at short and intermediate times are seen. Quite reasonable agreement is observed with the predictions of the DE model, especially when allowance is made for the self-consistent motion of the surrounding chains.

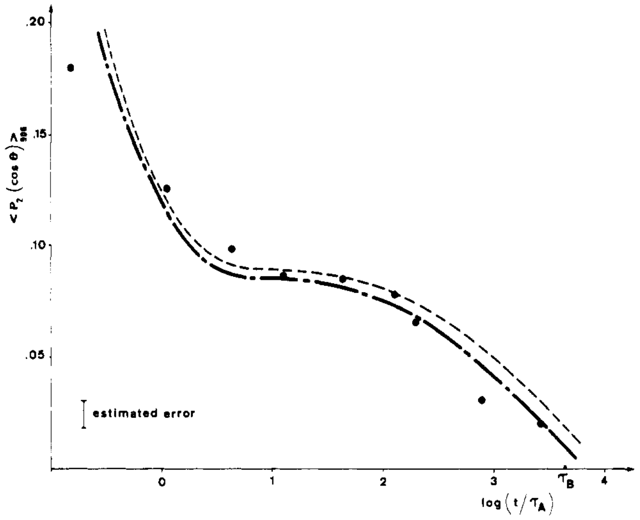

Figure 2. Orientation function vs time for polystyrene PS2 compared with theoretical predictions (- - -, free chain in a fixed network; –·–, self-consistent treatment).

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Registry No. PS, 9003-53-6.

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Permeation of Aqueous KBr through Langmuir-Blodgett Films of Singly and Doubly Polymeric Monolayers

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We describe herein the permeation experiment of aqueous KBr across Langmuir–Blodgett (LB) films deposited on a porous polymer film. The gas permeation characteristics of the LB films have been examined by several groups, because of their unique structures as very thin films of ordered molecules. Rose and Quinn[2] showed in their pioneering study that the rate of gas permeation was reduced by a built-up multilayer film of stearic acid.

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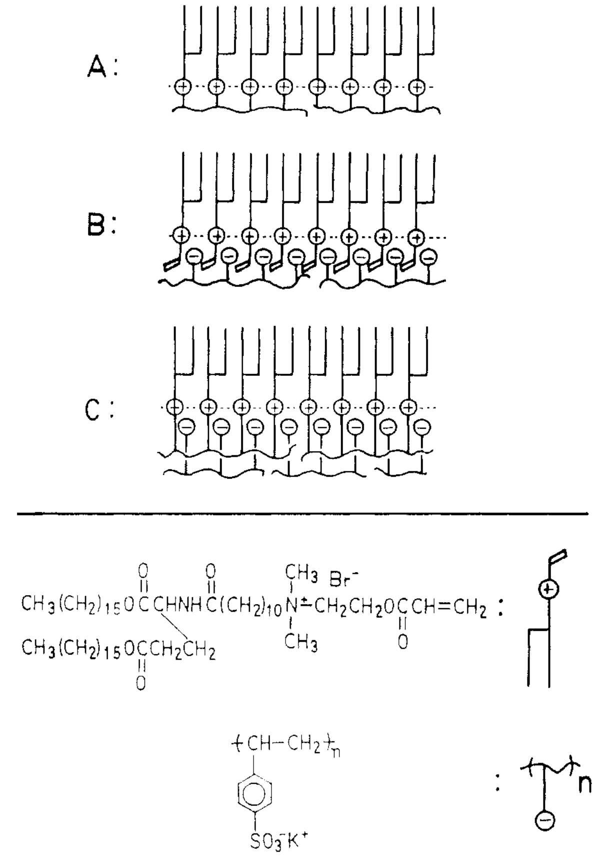

Figure 1. Three types of the polymeric monolayer: (A) monolayer of prepolymerized amphiphile; (B) polyion complex of unpolymerized monolayer; (C) polyion complex of polymerized monolayer. This is produced either by postpolymerization of a type-B monolayer or by spreading of a prepolymerized monolayer (type A) on aqueous polyanion.

Similar rate reductions were observed by Gaines and Ward[3] and by Ringsdorf and co-workers.[4] We recently reported oxygen enrichment by using LB films of fluorocarbon amphiphiles.[5,6]

The permeation experiment of molecules and ions in solution is more difficult, since very thin LB films quickly disintegrate in water or in organic solvents. A few years ago, Kajiyama et al.[7] found that LB films of a double-chain ammonium amphiphile which were deposited on a polymer film displayed interesting permeation behavior for aqueous KBr, although the stability of the LB film was not thoroughly examined.

Polymeric LB films have been studied extensively in order to improve the film stability;[8] however, there are no published data on LB films of satisfactory stability in water. In the present study, we incorporated "the polymeric property" into the LB film by three different methods, as shown in the form of monolayers in Figure 1. One is the use of a polymerizable amphiphile, which is polymerized as aqueous bilayer dispersions, spread on water, and transferred onto a solid support. A second method is the use of polymer anions as counterion of ammonium monolayers, which is then transferred as polyion complexes.[9,10] A third approach is combinations of these methods: (a) unpolymerized ammonium amphiphile is spread on aqueous polyanion, deposited on a solid support, and then photopolymerized; (b) polymerized ammonium amphiphiles are spread on aqueous polyanion and deposited. The third approach produces doubly polymeric monolayers with dense networks of salt bridges. Attempted stabilization of monolayers by chemical cross-linking was discussed by Bauer and others.[11]

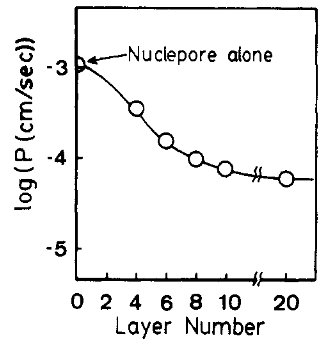

Figure 2. Dependance of the apparent permeation rate on the number of deposited molecular layers. Postpolymerized LB films (type C) deposited on a Nuclepore film are used at 20 °C against 10 mM aqueous KBr.

Amphiphile 1 is a typical double-chain amphiphile that forms bilayers in water.[12] It also forms stable monolayers at the air–water interface, as inferred from its surface pressure–area isotherms which are measured with a microprocessor-controlled film balance and lifter (San-esu Keisoku Co., Model FSD 20 and FSD 30). Deposition of the surface monolayer onto the one side of a porous polycarbonate film (Nuclepore NP-300, pore size 0.03 μm, Nomura Micro Science Co., Ltd.) was performed with or without poly(styrenesulfonate) in the subphase at surface pressures (25–30 $mN \cdot m^{-1}$) where the monolayers were in the condensed phase.[13] The Y-type LB films thus obtained were, where necessary, sealed in evacuated ampules and irradiated at 0 °C with a 1-Mrad γ-ray from a ^{60}Co source. The permeation experiment was carried out between pure water and 10 mM KBr with a conventional, thermostated, H-shaped cell. The Nuclepore films were set so that the LB multilayer faced aqueous KBr. The rate of KBr permeation was estimated from the initial slope of conductivity increase of the water side.

Figure 2 summerizes the permeation data with postpolymerized LB films of a polyion complex. The apparent permeation rate, P (cm/s), is suppressed relative to that of a Nuclepore film alone, even by deposition of the four monolayers (two deposition cycles), and is further lowered with increasing layers. The rate decrease becomes less significant beyond 10 layers. It appears that 10 molecular layers is sufficient to cover all the pores in the polymer film. Preliminary scanning electron microscopic study indicated that the pores in a Nuclepore film become unobservable at this stage of deposition. This permeation barrier was maintained after repeated experiments at different temperatures (up to 60 °C). Without γ-ray polymerization, however, the resistance against ion permeation was mostly lost when the experiment was repeated.

Other "polymeric" LB films also displayed satisfactory stabilities under similar conditions. Deposition (10 monolayers) of the prepolymerized monolayer of 1 (aqueous bilayer dispersion of 1 was polymerized by UV irradiation) gave repeatable permation rates (log P) of −3.4 at 30 °C. Aging of this film in water at 60 °C lowered log P to −4.3. The LB film of a postpolymerized polyion complex (see Figure 1) gave log P of −4.1 at 30 °C, which did not change upon aging. When the prepolymerized amphiphile was spread on aqueous poly(styrenesulfonate), the least permeable LB film (10 monolayers) was obtained with log P of −4.8. This value is close to the lower limit of the observable permeation rate (log P = −5 to −6).

In conclusion, we could demonstrate that polymeric LB films (10 monolayers) were stable enough in water as a permeation barrier. The two-dimensional network of salt bridges which is formed in polyion complexes of polym-

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erized monolayers was particularly efficient for enhancing the barrier capacity of very thin multilayers.

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Sensitivity of Ternary Phase Diagrams of Miscible Polymer Pairs in Common Solvents to Traces of Water: Solvent–Poly(ethyl acrylate)–Poly(vinyl propionate) and Solvent–Poly(methyl acrylate)–Poly(vinyl acetate) Systems

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A miscible polymer pair in a common solvent gives rise to clear solutions at all compositions, or the triangular phase diagrams of the solvent (1)–polymer (2)–polymer (3) contain closed immiscibility loops.[1-3] Quite a few of these diagrams have been published in the literature.[3-9] The miscibility of closely similar polymer pairs has been studied in this laboratory for some time.[7,10,11] The phase diagrams of solutions of one such pair, poly(methyl acrylate) (PMA)–poly(vinyl acetate) (PVAc), in solvents such as toluene and 1,2-dichloroethane have been published from this laboratory by Nandi et al.[7] The phase diagrams contained closed immiscibility loops. While continuing these studies using an analogous miscible polymer pair, poly(ethyl acrylate) (PEA) and poly(vinyl propionate) (PVPr), we discovered that traces of water which remain in the systems under the usual experimental conditions, unless extremely stringent precautions are taken, bring about inhomogeneity in some of the ternary solutions at subambient temperatures. The closed immiscibility loops observed in the phase diagrams in the paper of Nandi et al. referred to above resulted from the presence of traces of water in the systems. Under the stringently dry conditions these do not appear. In this note we report the results of phase studies for the miscible polymer pair PEA + PVPr in common solvents with special reference to the effect of traces of water on the homogeneity of the ternary solutions.

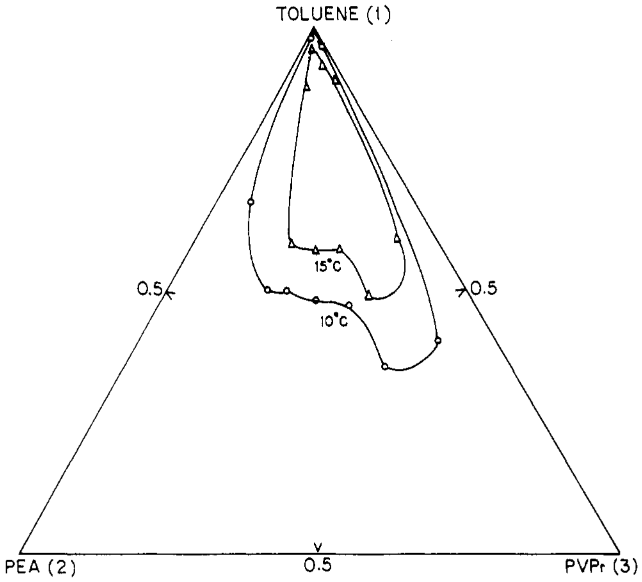

Figure 1. Ternary phase diagram of toluene (1)–PEA (2)–PVPr (3) at the indicated temperatures (normal sealing technique).

Experimental Section

PEA ($\bar{M}_n$ = 773 000) and PVPr ($\bar{M}_n$ = 34 700) were whole polymers prepared in the laboratory.[10] The solvents used were of analytical reagent grade. They were purified by standard methods,[12] dried over Drierite, and distilled before use. Two different procedures were adopted for making the ternary solutions. In the first method (the normal technique), a polymer blend (blended by dissolution in a common solvent and casting film) was weighed into a tared dry Corning glass tube (7 mm × 20 cm), the required amount of a dry solvent was added, and the tube was sealed without cooling the solvent. The small loss of solvent during sealing was determined from the weights of the sealed-off parts and the initial weights and due correction in composition was made. In the second method (vacuum line transfer technique), dry and degassed (freeze–thaw process) solvent was stored over Drierite (with indicator) in one section of a greaseless vacuum manifold. A polymer blend was weighed into a tared Corning glass tube (7 mm × 20 cm) provided with a flange. The tube was attached to the vacuum line through a flange joint, evacuated to $\sim 10^{-6}$ Torr, and pumped for 1 h. The solvent was then transferred into the tube from the reservoir to a predetermined level. The tube was then sealed. The sealed-off parts were weighed, and the amount of solvent transferred was estimated from these weights and the initial weight of the tube with the polymers.

The tubes sealed by both methods were kept at 70–80 °C for 4 days to ensure dissolution of the polymers. They were then slowly cooled, and the cloud points were visually noted as reported previously.[7]

Results and Discussion

The common solvent solubility of the blends was studied in the following solvents; ethyl acetate, ethyl propionate, acetone, methyl ethyl ketone, chloroform, benzene, 1,2-dichloroethane, toluene, and chlorobenzene. First, the clarity of the solutions of the 1:1 blend at 10 and 50 wt % concentrations prepared by the normal sealing technique was examined. The solutions were found to remain clear over the temperature range −30 to 100 °C except for toluene and chlorobenzene, where cloudy solutions were obtained at subambient temperatures. The cloud points of solutions of various other compositions in these two solvents were then determined, and the phase diagrams shown in Figures 1 and 2 were constructed. These diagrams were very similar to those obtained by Nandi et al. for the solvent–PMA–PVAc system and may be explained

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