Photocontrol of Polypeptide Membrane Functions by Cis–Trans Isomerization in Side-Chain Azobenzene Groups

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ABSTRACT: A photoresponsive polypeptide membrane has been prepared by casting a chloroform solution of poly(L-glutamic acid) (PGA) with azobenzene groups in the polymer side chains (azo-modified PGA). The azo-modified PGA membrane exhibited an α-helix CD pattern. The azobenzene side chains in the solid membrane exhibited trans to cis photoisomerization under UV light irradiation, which was completely reversed in the dark. Irradiation, however, did not induce any conformational changes of the polymer backbone. The water content of the membrane was found to increase by UV irradiation owing to a polarity change of the azobenzene moieties based on their photoisomerization. This increase in the hydration of the membrane resulted in the acceleration of acid dissociation of the L-glutamic acid moiety. As a result, the membrane potential across the membrane was increased by UV irradiation, indicating an increase in the negative charge of the membrane. The cross-membrane conductance through the membrane was found to be changed by UV irradiation, depending on the KCl concentration in the bulk solution. The changes in the cross-membrane conductance can be explained in terms of enhancement of the diffusibility of ions and the acceleration of acid dissociation (Donnan exclusion effect) via an increase in the water content of the membrane by UV irradiation. The photoinduced changes of the membrane potential and the permeability were reversible and in correlation with the change in absorbance of the azobenzene groups at 350 nm.

The control of polymer membrane functions has been studied extensively over the years to determine the application of polymer membranes to an energy conversion media. It has been recognized that natural membrane activities, such as transport properties, membrane potentials, and binding abilities to small molecules, can be drastically changed by conformational changes of macromolecules in the membranes, which are induced by environmental change. In previous studies, we have shown that transport properties of polypeptide membranes can be controlled by pH-induced α-helix to coil transition of poly(L-glutamic acid)[1-3] and redox-controlled conformational changes of poly(L-cysteine)[1] in the membranes. Investigations on such an external stimulus-responsive membrane are of great importance in membrane technology and science.

Recently, much effort has been made in the characterization of the photoresponsive properties of membranes entrapping photochromic compounds such as azobenzene and spiropyran derivatives. Aizawa et al.[4-7] have shown that the membrane potential across cellulose acetate membranes could be controlled by the photoinduced change in the charge density of a membrane-bound spiropyran and a retinal. Anzai et al.[8,9] used the cis–trans isomerization of azobenzene-modified crown ethers to regulate the membrane potential across a poly(vinyl chloride) membrane. The photocontrol of the membrane permeabilities has been also reported by many researchers. Spiropyran derivatives have been utilized to photocontrol the membrane permeabilities through liposome[10] and cellulose acetate membranes.[11] Photoinduced trans–cis isomerization of azobenzene derivatives has also been widely utilized to photocontrol metal ions permeabilities through poly(vinyl chloride) membranes,[12,13] liquid crystalline membranes,[14] liposome,[15] and bilayer membranes.[16] More recently, it has been shown that the membrane potentials and permeabilities of polymer membranes containing photochromic compounds in the polymer chains could be regulated by light irradiation. Irie et al.[17] have shown the photocontrol of the membrane potentials across poly(methyacrylic acid) membranes in a low ionic concentration region caused by a charge density change of the membrane via the photoisomerization of spiropyran pendant groups. Moreover, Ishihara et al.[18,19] have shown that organic compound and protein permeabilities through the membrane of poly(2-hydroxyethyl methacrylate) containing azobenzene groups in the side chains could be reversibly regulated by photoirradiation based on the contraction of the swollen membrane caused by a photoinduced polarity change of the azobenzene groups.

We report here on the photoresponsive behavior of polypeptide membrane composed of poly(L-glutamic acid) containing azobenzene groups in the side chains based on a cooperative effect between the photoisomerization of the azobenzene moiety and acid dissociation of glutamic acid groups in the membrane. Primary results of the photoresponsive membrane properties of the azomodified PGA were reported previously.[20,21]

Experimental Section

Details in synthesis and characterization of the photoresponsive properties of the polymer in solution have been already reported by Ciardelli et al.[22-24] PGA polymers with incorporated azobenzene groups (azo-modified PGA) were synthesized by the condensation reaction of PGA ($\bar{M}_v = 1.19 \times 10^5$) with *p*-aminoazobenzene in dimethylformamide at 70 °C, as reported by Ciardelli et al.[22] The azobenzene content in the polymers obtained was determined from the absorbance at 350 nm of the chloroform solution of the azo-modified PGA on the basis of the molar extinction coefficient of the trans form of *p*-aminoazobenzene in chloroform. The maximum mole percent of the azobenzene moieties in the polymer obtained was 14 mol %. A membrane of ca. 10-μm thickness was prepared for the membrane potential measurements by casting a 2% chloroform solution of the azo-modified PGA on a flat glass plate and allowing the solvent to evaporate. For permeation (cross-membrane conductance) measurements, a membrane of ca. 1.0-μm thickness was prepared by coating a porous filter (Millipore filter, pore size 0.1 μm) with a 2% chloroform solution of the polymer and allowing the solvent to evaporate.

Irradiation was carried out with a 100-W high-pressure mercury lamp (Rico-Kagaku Sangyo Co. Ltd., UVL 100P).

Absorption spectra of the membrane were measured with a spectrophotometer (Shimadzu Co. Ltd., UV-200). A membrane of 1.0-μm thickness was prepared by coating the inner surface of a UV cell with the azo-modified PGA. The temperature of the cell was controlled by circulating thermoregulated water with a Komatsu-Yamato CTR-220 thermobath.

CD and IR spectra of the membrane were measured with a spectropolarimeter (Jasco, J-40) and a diffracting grating infrared spectrometer (Jasco, IRA-2), respectively. The measurements were carried out by using a water-containing membrane, adapted

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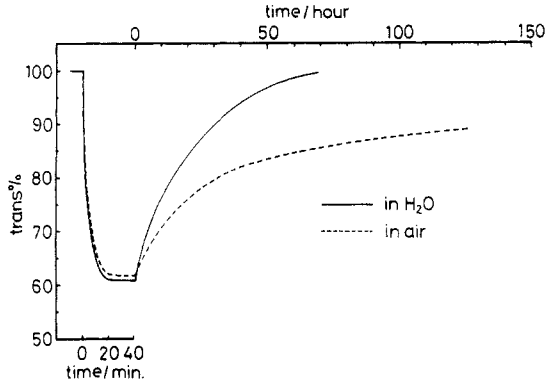

Figure 1. Changes in *trans*-azobenzene content of an azo-modified PGA membrane containing 14 mol % azo groups at 25 °C: (—) membrane in water; (– – –) dry membrane.

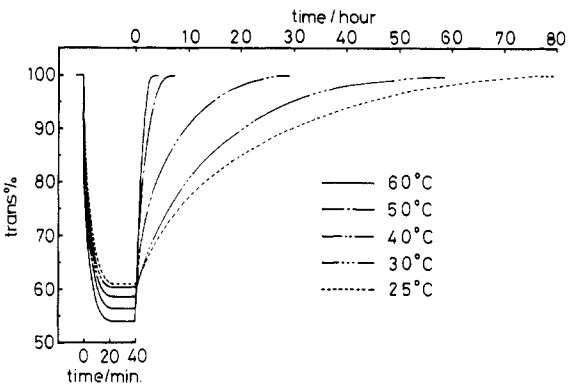

Figure 2. Temperature dependence of changes in *trans*-azobenzene content of an azo-modified PGA membrane containing 14 mol % azo groups in water.

in the dark or irradiated. CD data are expressed in terms of ellipticity θ_λ, since the molar ellipticity could not be obtained at present because of the uncertainty in the thickness and density of the water-containing membrane.

The water content of the membrane (H, weight fraction of water in the water-swollen membrane) was determined at 25 °C. The membrane was swelled in the dark and under UV irradiation, respectively, blotted and weighed until constant weight was obtained, and then dried under reduced pressure. The H value was calculated from the difference of the weights.

The cell circuit for the determination of membrane potentials, $\Delta(\Delta\psi)$, is represented by

$$\underset{1}{\text{Ag·AgCl|sat KCl|}C_1\text{|membrane|}C_2\underset{2}{\text{|sat KCl|Ag·AgCl}}$$

where Ag·AgCl is the Ag·AgCl electrode and junctions 1 and 2 were connected by salt bridges. In this case, C_1 and C_2 ($C_1 > C_2$) are the KCl concentrations, and the potential of the higher KCl concentration (C_1) side was taken as zero. The KCl concentration ratio C_1/C_2 was fixed at 4. The membrane potential measurements were performed at 60 °C.

The measurement of cross-membrane conductance was carried out by using a Pyrex glass permeation cell with platinum black electrodes at 60 °C. The KCl concentration in both sides of the membrane was fixed to 1.0 mol·dm^{-3} and 1.0 × 10^{-4} mol·dm^{-3}, respectively. The conductances were measured with a conductance meter (TOA electronics Co. Ltd., CM-5B). The cross-membrane conductance, κ_{KCl}, was expressed as the apparent value of the conductance obtained.

Results and Discussion

Photoisomerization. Azobenzene is known to change its absorption spectrum when the configuration changes from the trans to the cis form. Ciardelli et al.[24] have shown that a main absorption band of the azo-modified PGA in solution at 340 nm due to the π–π^* transition decreases while a weak band at 450 nm due to the n–π^* transition increases upon UV irradiation. In the solid membrane in water, the photoisomerization was characterized by the changes in the absorption bands at 350 and 450 nm, respectively. On the basis of the changes in the absorbance at 350 nm, it was estimated that 38% of the trans form was converted into the cis isomer in the membrane in water at 25 °C. In chloroform and trimethyl phosphate solutions, higher photoconversion ratios are observed;[24] however, the photoconversion in the solid membrane is the same as that in aqueous solution.[24] This result may imply that the configurational change of the azobenzene moiety occurs easily even in the solid membrane. In a dry sample of the azo-modified PGA membrane, a slightly lower photoconversion ratio is obtained at 25 °C (ca. 36%). Figure 1 shows the changes in the trans form content in the membrane at 25 °C by on–off switching of the UV lamp. It is clear that the half-life of the metastable cis isomer in a dry membrane is much longer than that in a wet membrane. The temperature effect on the changes in the trans content in membrane in water is shown in Figure 2. The trans–cis photoconversion is slightly increased by temperature; i.e., 45% of the trans form was converted into the cis isomer at 60 °C. Furthermore, markedly faster thermal (dark) relaxations (cis–trans isomerization) can be obtained at higher temperature. The temperature dependence of the rate of the thermal relaxation as the reciprocal of the half-life of the cis isomers, $1/t_{1/2}$, is shown in Figure 3. Figure 3 shows that the rate of the thermal relaxation is discontinuously increased above 40 °C. Eisenback[25] have reported that the cis–trans isomerization processes of poly(methacrylate) films containing azobenzene side chains are associated directly with relaxation phenomena of the polymer matrix. Therefore, the inflection point at 40 °C in Figure 3 may correspond to the secondary transition temperature of the side chains in the azo-modified PGA membrane. The activation energies below and above 40 °C obtained from Figure 3 are 17.5 kJ·mol^{-1} (4.20 kcal·mol^{-1}) and 41.6 kJ·mol^{-1} (9.94 kcal·mol^{-1}), respectively. The activation energies of the thermal relaxation of azobenzene groups in bulk poly(methacrylates)[25] below and above T_g were shown to be 6–17 kcal·mol^{-1} and 20–30 kcal·mol^{-1}, respectively. The lower activation energies of the thermal relaxation in the azo-modified PGA membrane may also support the fact that the configurational changes of azobenzene side chains occurs easily in the solid membrane of the α-helical polypeptide.

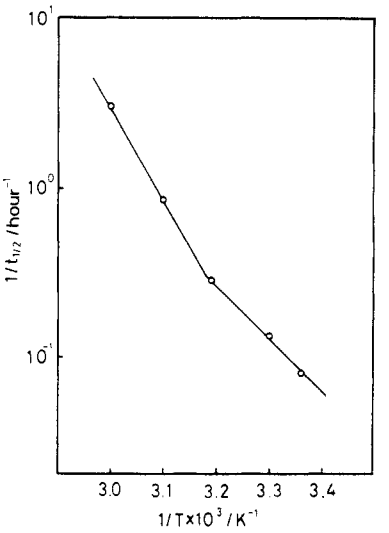

Figure 3. Arrhenius plot of the reciprocal of half-life of *cis*-azobenzene side chains in an azo-modified PGA membrane containing 14 mol % azo groups in water.

Table I
Photoinduced Changes in Membrane Functions of Azo-Modified PGA

	in the dark	UV irradiation
H^a (25 °C)	0.163	0.200
$\phi X/K_\pm{}^b$ (60 °C), mol/L	2.31×10^{-3}	3.86×10^{-3}
$\kappa_{KCl}{}^a$ (1.0 mol/L, 60 °C), mS/cm	11.2	13.2
$\kappa_{KCl}{}^a$ (1.0×10^{-4} mol/L, 60 °C), μS/cm	26.4	26.7

[a] Azo-modified PGA containing 12 mol % azo groups. [b] Azo-modified PGA containing 14 mol % azo groups.

Backbone Conformation. The photoinduced conformational changes of polypeptides were first accomplished by Ueno et al.[26-34] with azobenzene-containing poly(aspartates) in solution. They have found that photoresponsive poly(aspartates) can undergo a photoinduced conversion of the secondary structure in solution. However, they[35] also reported that the backbone conformation of azobenzene-containing poly(aspartates), which undergo a photoinduced conformational transition in solution, could not be changed by irradiation in the solid membranes. Ciardelli et al.[24] studied the water-soluble azo-modified PGAs in an aqueous solution and reported photoinduced α-helix ⇄ coil and β-structure → coil transitions that depend on the azo group content and pH value of the aqueous solution at which irradiation is carried out. The CD spectra of the azo-modified PGA solid membrane containing 14 mol % azo groups, which are adapted in the dark or irradiated in water (pH 6.2), revealed that the UV irradiation does not induce any changes of the backbone conformation of the membrane. This result is consistent with the fact[24] that the conformation of the water-soluble azo-modified PGA having a low azo group content (16 mol %) in an aqueous solution is almost insensitive to UV irradiation at any pH value.

Water Content of the Membrane. Water content of the azo-modified PGA membrane, H, in the dark is shown in Table I. The small H value suggests that the polymer is much less hydrophilic than expected, in spite of a large content of COOH groups. Ambrose[36] has indicated the presence of hydrogen bonding between side-chain COOH groups in the solid membrane of poly(glutamic acid). We[37] have also shown that methyl glutamate (hydrophobic)–glutamic acid copolymers contain an appreciable amount of hydrogen bonding between COOH side chains, even in the copolymer having a lower glutamic acid content. In addition, Houben et al.[38] have pointed out the presence of apolar *N*-acylureic groups in the water-insoluble azo-modified PGA, while the water-soluble azo-modified PGA does not contain the hydrophobic units. The procedure used in this study to introduce azo groups, therefore, may also give rise to the formation of nonpolar *N*-acylureic groups in the polymer obtained. These results can explain the low H value in Table I and insolubility of the polymers in aqueous solution and also imply that the content of free COOH groups in the polymer is very low. Changes in the water content of the azo-modified PGA membrane by UV irradiation are shown in Table I. The enhancement of water uptake in the membrane upon irradiation was observed. Azobenzene is known to change its polarity during photoisomerization, since the apolar trans form is converted into the more polar cis isomer upon UV irradiation. This increase in the water content of the membrane, therefore, may be associated with a decrease in the hydrophobicity of the side-chain azobenzene groups. On the other hand, a photoinduced decrease in the water content of the membrane was also observed by Ishihara et al.[18,19] and Matějka et al.[39] using poly(2-hydroxyethyl methacrylates) containing azobenzene side chains. This decrease in the water content of the membrane was explained in terms of the dehydration from the hydroxy groups in the membrane due to the interaction between the hydroxy group and the polar *cis*-azobenzene moiety based on the photoinduced polarity change. As described previously, the content of free COOH groups, which easily interact with polar cis isomers, is very low in the azo-modified PGA membranes used. It seems, consequently, that the polarity change of side-chain azobenzene groups by irradiation simply resulted in the enhancement of water uptake by the membrane.

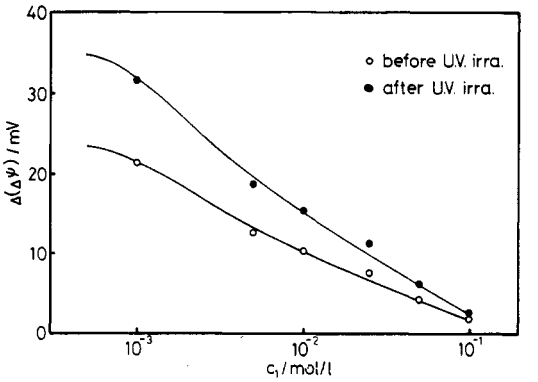

Figure 4. KCl concentration dependence of membrane potentials of an azo-modified PGA containing 14 mol % azo groups at 60 °C.

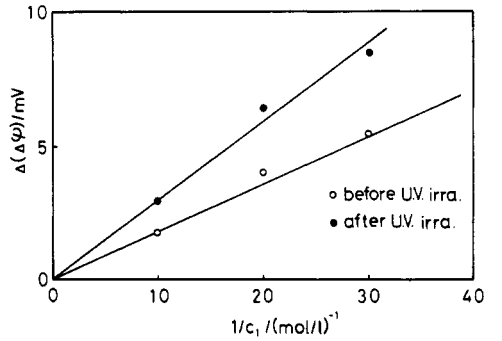

Figure 5. Relationship between membrane potentials of an azo-modified PGA containing 14 mol % azo groups and $1/C_1$ (eq 1).

Membrane Potential and Cross-Membrane Conductance. The dependence of the membrane potential, $\Delta(\Delta\psi)$, of the azo-modified PGA membrane containing 14 mol % azobenzene groups on UV irradiation was observed at pH 6.2 with a KCl concentration gradient of $C_1/C_2 = 4$ at 60 °C. A positive shift of the membrane potential was observed when the membrane was irradiated with UV light at 60 °C, and it was required for about 10 min to attain a steady-state potential (Figure 4). According to Teorell–Mayer–Sievers theory,[40-42] the membrane potential is given for membrane–KCl systems ($\bar{l}_{K^+} = \bar{l}_{Cl^-}$) in the high external concentration region as[42]

$$\Delta(\Delta\psi) = \frac{RT}{F}\frac{\phi X}{2K_\pm}(r-1)\frac{1}{C_1} \qquad (1)$$

where $\bar{l}_i$ is the mobility of the ith ion in the membrane, ϕX is the effective (negative) charge density of the membrane, $K_\pm$ is the equilibrium partition coefficient, $r = C_1/C_2$, and R, T, and F are commonly used notations. Applying eq 1 to the plot in the high-concentration region in Figure 4, we can estimate the photoinduced change in the charge density of the membrane, $\phi X/K_\pm$ (Figure 5). The result is shown in Table I. Irradiation produces an increase in the negative charge density of the membrane,

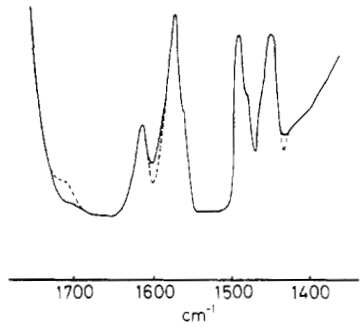

Figure 6. IR spectra of a water-swollen azo-modified PGA membrane containing 14 mol % azo groups: (—) in the dark; (---) UV irradiation for 30 min.

suggesting an increase in the degree of dissociation of the L-glutamic acid moiety in the membrane by UV irradiation. As shown in a preliminary communication,[21] the trans–cis isomerization of the azobenzene group in the membrane does not directly affect the membrane potential, since the $\Delta(\Delta\psi)$ value of the azobenzene monomer entrapped poly(γ-methyl L-glutamate) membrane was independent of UV irradiation. Furthermore, IR spectra of the water-containing membrane containing 14 mol % azo groups adapted in the dark or irradiated are shown in Figure 6. The noticeable differences between the two spectra are observed in absorption bands at 1720, 1600, and 1430 cm^{-1}. The absorption band at 1720 cm^{-1} is due to the C=O stretching mode of the hydrogen-bonded carboxy group in the side chains.[36,37] On the other hand, the bands at 1600 and 1430 cm^{-1} are attributable to the C–O stretching modes of the dissociated COO^- groups of the side chains. It is clear, from Figure 6, that irradiation produces an increase in the degree of dissociation of the L-glutamic acid. In addition, we[43,44] have shown that the membrane potentials of partially charged polypeptide membranes containing hydrophobic moieties steeply increase with a slight increase of the amount of dissociable group, especially in the hydrophobic unit rich membrane. The hydrophobic nature of the azo-modified PGA, which may be due to apolar *N*-acylureic groups, therefore, may effectively amplify a photoinduced change of the membrane potential via the small increase in the charge density of the membrane on UV irradiation. These results suggest that the acid dissociation in the membrane is accelerated, accompanied by an increase in the polarity of and the enhancement of water uptake by the membrane upon the formation of polar cis isomers with UV irradiation. The pK_a value of the L-glutamic acid moiety in the irradiated membrane is lower compared with that of the membrane adapted in the dark. Ciardelli et al.[24] have also suggested that the higher polarity of the cis isomer induces an easier acid dissociation of the neighboring COOH side groups of the water-soluble azo-modified PGA in an aqueous solution. Thus, the photoinduced increase in the membrane potential can be explained in terms of the cooperative effect between the photoreaction of the azobenzene group and the induced dissociation of L-glutamic acid moiety in the membrane accompanied by the enhancement of water uptake by the membrane on UV irradiation. Figure 7a shows an increase and recovery cycle of the membrane potential of the azo-modified PGA membrane containing 14 mol % azo groups. The photoinduced change of the membrane potential is closely related with absorbance change of the membrane at 350 nm (Figure 7c). Figure 7b shows the dependence of the cross-membrane conductance using KCl solution, κ_{KCl}, on UV irradiation for the membrane containing 12 mol % azo groups at 60 °C.

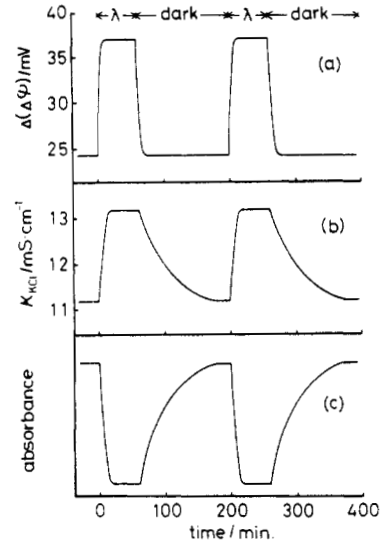

Figure 7. (a) Photoinduced membrane potential changes of an azo-modified PGA membrane containing 14 mol % azo groups at 60 °C; (b) photoinduced cross-membrane conductance changes of an azo-modified PGA membrane containing 12 mol % azo groups at 60 °C; (c) changes in absorbance at 350 nm of an azo-modified PGA membrane containing 12 mol % azo groups in water at 60 °C.

UV irradiation gave a positive shift of κ_{KCl} when the KCl concentrations were same (1.0 mol·dm^{-3}) at both sides of the membrane. Conversely, the enhancement of κ_{KCl} was only 2% when the ionic strength was 1.0×10^{-4} mol·dm^{-3} (Table I). As described previously, the enhancement of water uptake by the membrane due to UV irradiation accelerates acid dissociation in the polymer side chain. In addition, the space in the membrane is also increased by the enhancement of water uptake by the membrane. The acceleration of the acid dissociation in the membrane decreases the solubility of ions to the membrane according to the Donnan exclusion effect.[43] On the other hand, the swelling of the membrane due to the enhancement of the water uptake by the membrane increases the diffusion of ions through the membrane. Therefore, the positive shift of κ_{KCl} at high ionic concentration (1.0 mol·dm^{-3}) can explained by the membrane swelling upon UV irradiation. On the other hand, the decrease in the solubility of ions to the membrane may result in the slight increase in the κ_{KCl} value in low ionic concentration (1.0×10^{-4} mol·dm^{-3}), where the Donnan exclusion effect is predominant. Thus, when photostimulation was applied to the azo-modified PGA membrane, different changes in the conductance were observed depending on the concentration of the surrounding KCl solution. It is also clear that the photoinduced κ_{KCl} changes were entirely consistent with the absorption changes of the membrane at 350 nm. An additional important finding is that the photoinduced change in the membrane potential responds more rapidly than both the permeability and spectral changes (Figure 7). It seems that the photoinduced changes in the membrane potential may be owing to the surface potential changes accompanied by the rapid trans $\rightleftarrows$ cis isomerization of the azo groups at the surface of the membrane.[21]

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Registry No. Water, 7732-18-5.

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Interchain Electron Donor–Acceptor Complexes: A Model To Study Polymer–Polymer Miscibility?†

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ABSTRACT: Interpolymeric interactions based on electron donor–acceptor (EDA) complexes were used to study polymer miscibility. A new series of comblike polymers containing the electron donor carbazole moiety in the side chain, poly((*N*-alkylcarbazol-3-yl)methyl methacrylates) (PHMCM-*n*) with n = 1–16 (number of carbon atoms in the alkyl group), were synthesized, and their interpolymeric EDA complexes with an acceptor polymer, i.e., poly(2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate) (PDNBM), were studied by differential scanning calorimetry and compared with EDA complexes of poly(2-carbazol-*N*-ylethyl methacrylate) (PHECM). Blends of all donors and acceptor polymers show a single T_g as prepared, but only the lower homologues of the series are miscible under different thermal conditions. In the case of PHMCM-2 blends an endotherm of "decomplexation" is observed, and this system could be considered as one showing lower critical solution temperature. The glass-transition temperatures of the miscible systems depend on the composition of the blends and show large positive deviations from the weight-average values. This indicates the formation of thermally reversible cross-linked networks. Different equations available in the literature to correlate glass-transition temperatures of miscible blends with their composition were tested on these systems.

Introduction

Nonbonding type interactions are responsible in most cases for the self-organization of both natural and synthetic macromolecules. The current situation on the role of nonbonding interactions in chemistry has been recently discussed by Lord A. R. Todd: "Apart from consideration of the hydrogen bond, we organic chemists have really paid little attention to linkages other than purely covalent. I believe that it will be the duty of organic chemists in the future to study the weak, non-bonding interactions which are of enormous importance in the large natural macromolecules. Such studies will lead to a blossoming of organic chemistry in the future" (from Lord Alexander R.

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