(2) Schaap, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C.; *J. Am. Chem. Soc.* **1975**, *97*, 3741.
(3) Blossey, E. C.; Neckers, D. C. "Solid Phase Synthesis"; Dowden, Hutchinson, and Ross: E. Stroudsburg, PA, 1975.
(4) Marnet, L.; Neckers, D. C.; Schaap, A. P. In "Solid Phase Methods"; Jones, J. B., Ed.; Wiley: New York, 1976.
(5) Neckers, D. C. *CHEMTECH* **1978**, *8*, 108.
(6) Schaap, A. P.; Thayer, A. L.; Zakalika, K. A.; Valenti, P. C.; *J. Am. Chem. Soc.* **1979**, *101*, 4016.
(7) Tamagaki, S.; Liesner, C. E.; Neckers, D. C. *J. Org. Chem.* **1980**, *45*, 1573.
(8) Nilson, R.; Kearns, D. R. *Photochem. Photobiol.* **1974**, *19*, 181.
(9) Kautsky, H. *Trans. Faraday Soc.* **1939**, *35*, 3795.
(10) Kenley, R. A.; Kirshen, N. A.; Mill, T. *Macromolecules* **1980**, *13*, 808.
(11) For an extensive review, see: Braun, A. M.; Oliveros, E.; Maurette, M. T. *Bull. Dir. Etud. Rech., Electr. Fr., Ser. A* **1983**, 43–78.
(12) Buell, S. L.; Demas, J. N. *J. Phys. Chem.* **1983**, *87*, 4675.
(13) Lamberts, J. J. M.; Neckers, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 7465.
(14) Lamberts, J. J. M.; Neckers, D. C. *Z. Naturforsch.* **1984**, *39B*, 474–484.
(15) Lamberts, J. J. M.; Schumacher, D. R.; Neckers, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 5879.
(16) Pratte, J. F.; Webber, S. E. *Macromolecules* **1983**, *16*, 1188.
(17) Pratte, J. F.; Webber, S. E. *Macromolecules* **1983**, *16*, 1183.
(18) Phillips, D.; Roberts, A. J.; Touter, T. *Macromolecules* **1983**, *16*, 1593.
(19) Collart, P.; Demeyer, K.; Toppet, S.; De Schryver, F. C. *Macromolecules* **1983**, *16*, 1390.
(20) Holden, D. A.; Xiao-Xiu Ren; Guillet, J. E. *Macromolecules* **1984**, *17*, 1500.
(21) Urruti, E. H.; Kilp, T. *Macromolecules* **1984**, *17*, 50.
(22) Yuzhakow, V. T. *Russ. Chem. Rev.* (*Engl. Transl.*) **1979**, *48*, 1076.
(23) Moan, J. *Photochem. Photobiol.* **1984**, *39*, 445.
(24) Arbeloa, L. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1725.
(25) Arbeloa, L. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1735.
(26) Kenner, R. D.; Khan, A. U. *Chem. Phys. Lett.* **1977**, *45*, 76.
(27) Kenner, R. D.; Khan, A. U. *J. Chem. Phys.* **1977**, *67*, 1605.
(28) Paczkowski, J.; Neckers, D. C. *Macromolecules*, **1985**, *18*, 1245.
(29) Kamat, P. V.; Fox, M. A. *J. Phys. Chem.* **1984**, *88*, 2297.
(30) Kamat, P. V.; Fox, M. A. *J. Photochem.* **1984**, *24*, 285.
(31) Oster, G.; Adelman, A. H. *J. Am. Chem. Soc.* **1956**, *78*, 913.
(32) Adelman, A. H.; Oster, G. *J. Am. Chem. Soc.* **1956**, *78*, 3977.

Photoresponsive Polymers. 7.[1] Reversible Solubility Change of Polystyrene Having Pendant Spirobenzopyran Groups and Its Application to Photoresists

Masahiro Irie*

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan

Takao Iwayanagi and Yoshio Taniguchi

Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo, Japan.

Received March 29, 1985

ABSTRACT: The solubility of polystyrene in cyclohexane was found to change reversibly upon ultraviolet irradiation by incorporating small amounts (~2 mol %) of spirobenzopyran into the pendant groups. Photoisomerization of the pendant spirobenzopyran groups to the polar merocyanine form decreased polymer–solvent interaction, resulting in fractional precipitation of higher molecular weight polymers. The molecular weight of the precipitated polymer ($M_w = 5.1 \times 10^4$) was twice that of the soluble polymer ($M_w = 2.4 \times 10^4$) when the spirobenzopyran content was 3.9 mol %. The fractional precipitation behavior was interpreted through the change in the molecular weight dependence of the critical miscible temperature owing to the configuration of the pendant groups. The copolymer with a high content of spirobenzopyran groups (12.5 mol %) worked as a negative photoresist with high contrast.

Introduction

In a previous paper[2] it was reported that polystyrene with azobenzene pendant groups changes its solubility in cyclohexane upon irradiation with light of a specific wavelength; ultraviolet light caused precipitation of the polymer, while visible light resolubilized it. Structural changes of the pendant azobenzene groups from the trans to cis form altered the balance of polymer–polymer and polymer–solvent interaction, resulting in contraction of the polymer chain and finally in its precipitation. Time-resolved light-scattering intensity measurement after a laser flash in the microsecond time range yielded evidence for the polymer chain contraction (indicated by an increase of the scattering intensity) with a rate constant of 10^3–10^4 s^{-1}. The precipitation was observed at several hundred milliseconds after the flash.[3]

In the present article, we report a reversible solubility change of polystyrene with spirobenzopyran pendant groups in cyclohexane and its application to photoresists. Our first paper on photoresponsive polymers[4] has shown that poly(methyl methacrylate) with spirobenzopyran pendant groups changes the viscosity reversibly in benzene upon ultraviolet irradiation. The decrease of viscosity due to photogeneration of the merocyanine form was explained by the intramolecular solvation of merocyanines by ester side groups.

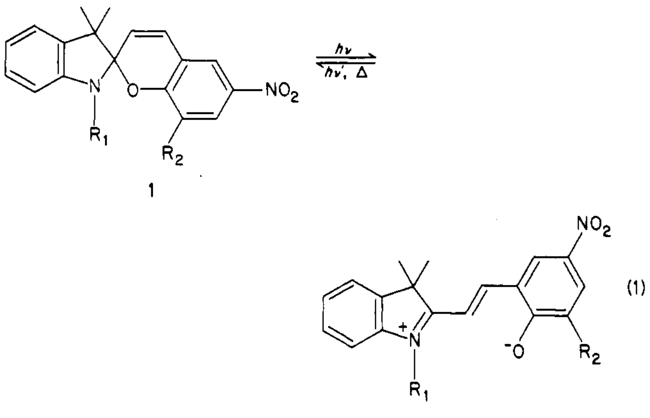
Recently, Goldburt et al.[5] and Kalinsky and Williams[6] have reported intramolecular stack formation among pendant merocyanine groups upon irradiation of polymers with spirobenzopyran pendant groups. In these experiments, the pendant groups are attached to the polymer at the N position through an ester linkage. This photochemically induced reaction is in contrast to our observation[4] where the methacryloxy methyl substituent is introduced at the 8′ position of the spirobenzopyran group. This suggests that steric factors play an important role in the behavior of merocyanine forms in weakly polarizable solvents such as toluene. Analysis of the behavior in nonpolar solvents, such as cyclohexane, will provide a new insight into understanding the photoresponsive mechanism of spirobenzopyran polymers.

Experimental Section

Spirobenzopyran chromophores were incorporated into the pendant groups of polystyrene by copolymerization with 1,3,3-

0024-9297/85/2218-2418$01.50/0 © 1985 American Chemical Society

trimethylindoline-2-spiro-2′-6′-nitro-8′-((methacryloxy)methyl)-benzopyran (1, R_1 = CH_3; R_2 = $CH_2OCOC(CH_3){=}CH_2$) by free-radical initiation.[4]



The content of spirobenzopyran in the polymer was determined by elemental analysis. The molecular weight distribution of the copolymer was estimated by gel permeation chromatography with a Toyo-Soda H801 high-speed liquid chromatograph. The molecular weight was estimated by comparison with polystyrene standard samples.

Irradiation was carried out with a 1-kW high-pressure mercury lamp, and the wavelength was selected to the ultraviolet (410 > λ > 310 nm) or visible (λ > 450 nm) region with the aid of Toshiba cutoff filters (UV-D2, UV-31, and UV-47). The polymer and monomer precipitation process upon irradiation was detected by measuring the decrease in the transmittance at 750 nm with a spectrometer (Shimadzu UV-200S). The temperature of samples was controlled with a temperature-controlled circulating bath (Neslab LT-50) and monitored by a digital thermometer (Doric 410A), controlled to 30 ± 0.5 °C.

Lithographic evaluation was carried out as follows.[7] The copolymer was spin-coated onto a silicon wafer to a thickness of 0.7–1.2 μm and prebaked at 60 °C for 20 min. Exposure was carried out in air with a 600-W Xe–Hg lamp. After exposure the polymer was postbaked at 100 °C for 5 min and then developed in cyclohexane–xylene (1:1 volume ratio) solution. The residual film thickness was measured with an interference microscope.

Results and Discussion

Solubility Change. Low molecular weight polystyrene having a small amount of pendant spirobenzopyran groups (less than 15 mol % of monomer units) is soluble in cyclohexane at room temperature, and the solution is transparent. Upon ultraviolet irradiation (410 > λ > 310 nm) of the cyclohexane solution containing the copolymer, the solution turned blue, became turbid, and exhibited strong light scattering. The appearance of the blue color indicates conversion of the pendant spirobenzopyran groups to the open-form merocyanines as eq 1. Prolonged irradiation caused precipitation of the copolymer. Visible light irradiation (λ > 450 nm) resolubilized the polymer precipitate, and the solution again became transparent.

The precipitation process was followed by measuring the decrease in transmittance at 750 nm, where the merocyanine has no absorption. Figure 1 shows the decrease in transmittance of a cyclohexane solution of polystyrene containing 1.6 mol % of spirobenzopyran units (PS–S-1.6) upon ultraviolet irradiation and the subsequent increase upon irradiation with visible light. The transmittance decreased immediately after ultraviolet irradiation and reached a plateau value in 40 s. Upon visible light irradiation, the transmittance returned to the initial value in 60 s. In the dark, it took about 20 min for the turbidity to disappear. The decrease of the turbidity in the dark is due to thermal reverse reaction back to the spiro form of the merocyanines and partly ascribable to sedimentation of large precipitated particles. The cycles of photostimulated precipitation and dissolution of the copolymer could be repeated more than 10 times.

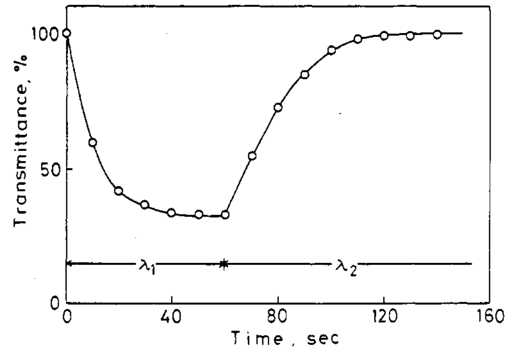


Figure 1. Changes of transmittance at 750 nm of cyclohexane solution containing PS–S-1.6 on alternate irradiation with ultraviolet light (410 > λ_1 > 310 nm) and visible (λ_2 > 450 nm) light. Concentration of the polymer was 0.070 g/dL.

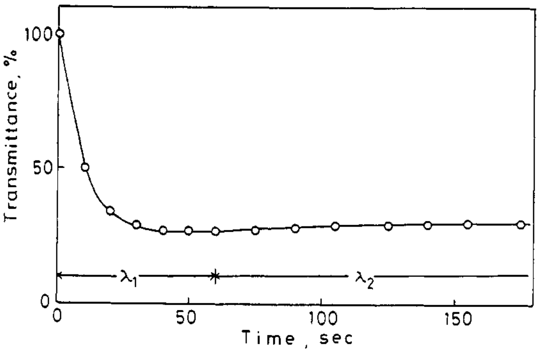


Figure 2. Changes of transmittance at 750 nm of cyclohexane solution containing monomeric spirobenzopyran on alternate irradiation with ultraviolet light (410 > λ_1 > 310 nm) and visible (λ_2 > 450 nm) light. Concentration of the spiro compound was 0.018 g/dL.

Although quantitative comparison of the precipitation process with the absorption spectral change was impossible because of scattering of the light by the precipitates, the deep blue coloration along with increased turbidity and subsequent disappearance of color with decreased turbidity upon appropriate irradiation indicate that the precipitation was caused by the isomerization of the pendant spirobenzopyran groups.

Figure 2 shows the photostimulated precipitation process of monomeric spirobenzopyran (R_1 = CH_3; R_2 = $CH_2OCOCH(CH_3)_2$) in cyclohexane measured by transmittance decrease at 750 nm. The transmittance decrease reached plateau in 40 s. The solution became red, and the transmittance remained constant even after visible light irradiation. This is in contrast to the behavior of polystyrene with pendant spirobenzopyran groups, as shown in Figure 1.

Photogenerated monomeric merocyanines are reported to make intermolecular stacks, A_nB (n = 1, 2, or 3; A, spiro form; B, merocyanine form), in aliphatic hydrocarbons. Further growth of the stacks results in the precipitation of the stacked crystals.[7] According to Krongauz,[8] dimer (AB) of 6′-nitrospirobenzopyran (R_1 = CH_3; R_2 = H) exhibits λ_{max} at 515 nm, while A_nB (n = 2, 3) have λ_{max} at 610 nm. The red precipitate from the monomer observed in this experiment gave strong absorption at 520 nm (Figure 3) and can be attributed to the aggregates, which consist of either AB or B_n with alternate antiparallel alignment of the molecular dipoles.[9] The strong dipole–dipole interaction and the lattice force of the crystals are believed to prevent the ring-closure reaction, merocyanine → spiropyran conversion, by visible irradiation.

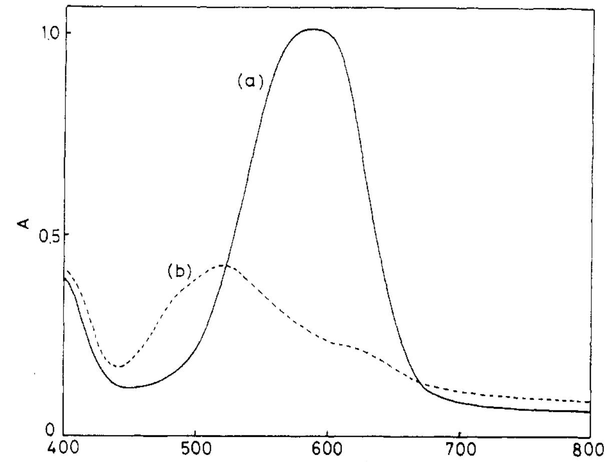


Figure 3. Absorption spectra of cyclohexane solution containing (a) PS-S-1.4 and (b) monomeric spirobenzopyran in the photostationary state under ultraviolet irradiation (410 > λ > 310 nm). The base-line shift is due to scattering by the precipitates. Concentrations of PS-S-1.4 and the monomeric spirobenzopyran were 0.070 and 0.005 g/dL, respectively. A cell with optical length of 0.5 cm was used.

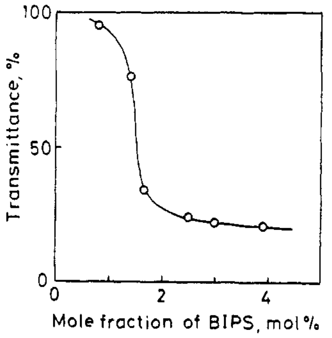


Figure 4. Dependence of transmittance at 750 nm in the photostationary state under ultraviolet irradiation (410 > λ > 310 nm) of polystyrene with pendant spirobenzopyran groups on the content of spirobenzopyran (BIPS) units in cyclohexane. Concentration of the polymer was 0.070 g/dL.

The fast, photostimulated merocyanine → spiropyran conversion of polymer pendant groups and the blue color of the precipitates (λ_{max} = 585 nm, Figure 3) suggest that merocyanine–merocyanine or merocyanine–spiropyran group interaction in the polymer system is different from that in the low molecular weight merocyanine aggregates. The interaction is considered to be very weak, and the precipitation of the polymer is mainly ascribable to the decrease of polymer–solvent interaction by the generation of polar pendant groups, as suggested in the case of polystyrene having azobenzene pendant groups.[2]

Figure 4 shows dependence of the amount of precipitate at a constant polymer concentration (0.070 g/dL) on the pendant spirobenzopyran content. Transmittance in the photostationary state under ultraviolet irradiation (410 > λ > 310 nm) sharply decreases when the content exceeds 1.5 mol % of monomer units. The change of the transmittance at very low spirobenzopyran contents indicates that isomerization of 4 spirobenzopyran units in a polymer of 200 monomer units in length (MW = 2×10^4) is enough to cause precipitation of the polymer. The critical content necessary to precipitate the polymer is much lower than that observed for the azobenzene polymer.[2]

Figure 5 shows the spirobenzopyran concentration dependence of the decrease of transmittance of a cyclohexane solution containing the copolymer with 2.5 mol % spirobenzopyran pendant groups as well as the solution of monomeric spirobenzopyran. The concentration dependence also suggests that the polymer precipitates by a mechanism different from that of monomeric spirobenzopyran. Isomerization of small amounts of pendant spirobenzopyran units is enough to cause the solubility change of the polymer in comparison with the monomeric spirobenzopyran. If the precipitation is caused by intra- or inter-molecular stack formation among the pendant merocyanines and spiropyrans, the pendant phenyl groups would sterically inhibit the precipitation. The styrene units of the copolymers, in contrast, assisted the precipitation. A very low concentration of spirobenzopyran is enough to cause the precipitation when they are incorporated into polystyrene. This result strongly suggests that the critical miscible condition of polystyrene in cyclohexane (Θ solvent for polystyrene) plays an important role in the precipitation process. In benzene, a good solvent for polystyrene, neither photostimulated precipitation nor conformational changes were observed.[4]

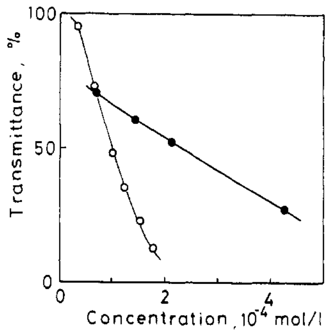


Figure 5. Concentration dependence of the transmittance decrease at 750 nm in the photostationary state under ultraviolet irradiation (410 > λ > 310 nm) of (○) PS-S-2.5 and (●) monomeric spirobenzopyran.

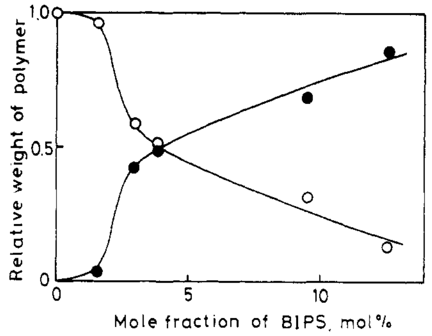


Figure 6. Spirobenzopyran (BIPS) content dependence on the amount of (●) photogenerated insoluble polymers by ultraviolet irradiation (410 > λ > 310 nm) of a cyclohexane solution containing polystyrene with pendant spirobenzopyran groups measured by gravimetry. (○) indicates soluble part. Concentration of the polymer was 0.070 g/dL.

When the content was less than 1 mol %, the precipitation was hardly observed, even in the polymer solution containing 0.2 g/dL. This also suggests that interstack formation of the pendant groups is not the primarily important factor of the precipitation.

Molecular Weight Distribution

In the preceding section, the precipitation process was followed by measuring the transmittance decrease at 750 nm. The decrease, however, could not give quantitative information on the amount of precipitate. Figure 6 shows the spirobenzopyran content dependence on the amount of photogenerated insoluble polymers measured by gravimetry. When the content exceeds 4 mol %, half of the dissolved polymer (0.070 g/dL) precipitated upon ultraviolet irradiation. More than 80% of the polymer pre-

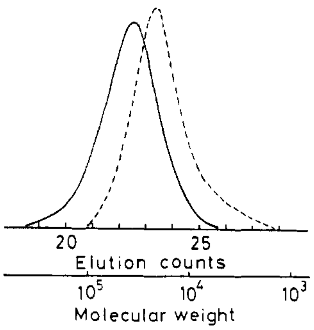


Figure 7. Molecular weight distribution of PS-S-3.9: (—) insoluble polymers in cyclohexane under ultraviolet irradiation (410 > λ > 310 nm); (- - -) soluble polymers.

cipitated when the copolymer contained 12.6 mol % of pendant spirobenzopyran units.

The difference in nature of the precipitate and the soluble polymer was compared with respect to the content of pendant spirobenzopyran groups and molecular weight distribution. The content of the spirobenzopyran units in the copolymer was measured by elemental analysis and by absorption spectral measurement. No significant difference in the copolymer composition was observed between the precipitate and the soluble polymer. This agrees well with the copolymerization theory that fluctuation of copolymer content is negligible in the copolymer prepared at low conversion.[10]

The molecular weight distribution, in contrast, was quite different between the precipitate and the soluble polymer. Figure 7 shows the molecular weight distribution of polymer containing 3.9 mol % pendant spirobenzopyran groups. The solid and broken lines show the molecular weight distribution of the precipitated ($M_w = 5.1 \times 10^4$, $M_w/M_n = 1.5$) and soluble polymer ($M_w = 2.4 \times 10^4$, $M_w/M_n = 1.6$), respectively. The result suggests that the precipitation behavior is similar to the fractional precipitation of a polymer from a solution by addition of a miscible nonsolvent.

The critical miscible temperature, T_c, below which the polymer precipitates, is expressed as follows:[10]

$$T_c = T_\theta(1 - b/M^{1/2})$$

where T_θ is the value of T_c at $M = \infty$ and b is an empirical constant. T_θ and b are assumed to change upon conversion of pendant spirobenzopyran groups to the merocyanine form. This is schematically illustrated in Figure 8, where T_c is plotted against $M^{-1/2}$. The photostimulated fractional precipitation can be interpreted by this relation. Before photoirradiation with all spirobenzopyran groups in the closed spiro form, all polymers with molecular weight $M_w < M_{w_s}$ are soluble in cyclohexane at T_M. Upon ultraviolet irradiation, the spiro form converts to the merocyanine form. Then, the polymers of $M_{w_m} < M_w < M_{w_s}$ become insoluble and precipitate from solution. The precipitation behavior suggests that the photoeffect is the same as lowering the temperature of the polymer solution from T_M to T_m. Formation of polar merocyanine groups in nonpolar solvent caused the decrease of polymer–solvent interaction, resulting in higher T_θ(m). This consideration leads to the conclusion that interpolymer dipole–dipole interaction is not the primary cause of precipitation, rather polymer–solvent repulsive forces play an important role in the precipitation process.

Intramolecular and intermolecular stacking, proposed by Krongauz and Williams to interpret slow merocyanine → spiropyran conversion for polymers with C-2 spacers in toluene and MTHF,[5,6] is assumed to make only minor contributions to the precipitation process in cyclohexane. The strong stacking force would not result in the fractional precipitation, but in the preferential precipitation of lower molecular weight polymers. Lower molecular weight polymers have higher diffusion constants and less steric hindrance toward the reaction among pendant groups. Both would accelerate the stack formation among lower molecular weight polymers. This was not the case and further substantiates the suggestion that fractional precipitation of higher molecular weight polymers induced by the decrease of polymer–solvent interaction occurs.

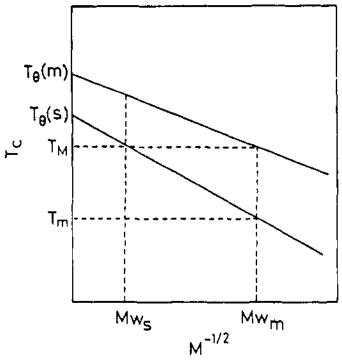


Figure 8. Molecular weight, M, dependence of critical miscible temperature, T_c. T_θ(s) and T_θ(m) indicate the values of T_c of polystyrene with spiro form and merocyanine form benzopyran pendant groups at $M = \infty$, respectively.

When the content of spirobenzopyran groups is small, as in the present experiment, the photogenerated merocyanines are considered to be self-solvated by the pendant phenyl groups in nonpolar cyclohexane. The contracted polymers aggregate to make the precipitates, as proposed for azobenzene polymers.[3] Such a weak interaction makes it possible to isomerize the merocyanines to the spiro form by visible irradiation. Once they made molecular stacks, strong lattice-force interactions would prevent photoisomerization of merocyanines to spiropyrans, as observed for the monomeric spiro compound.

Photoresist Applications

Photostimulated precipitation of the styrene copolymer, by as much as 80% (Figure 6), suggests its application to photoresist technology. In general, the differential dissolution rate of vinyl polymer resists is, so far, achieved through polymer backbone scissioning reactions (positive resists) or cross-linking phenomena (negative resists). Recently, Hofer and co-workers introduced a new design for negative resist action.[11] The new resist material, polystyrene with pendant tetrathiafulvalene groups, changed its dissolution rate through an alternation of the chemical nature of the groups by photogeneration of a tetrathiafulvalene bromide salt. The resist is reported to have a high contrast because of the absence of distortion by swelling.

The present polymer with pendant spirobenzopyran groups changes its solubility in cyclohexane by changing the polarity of the pendant groups. The nonpolar cyclohexane is assumed to selectively dissolve the polystyrene having the less polar spirobenzopyran pendant groups, but the solvent does not interact with the merocyanine-substituted polymer.

Figure 9 shows exposure characteristics for the copolymer along with a typical positive working resist of AZ 1350J. Although the copolymer having 12.5 mol % pendant spirobenzopyran showed very low sensitivity and contrast (curve a), the contrast was markedly improved by the addition of CBr_4 (curve b). The very low sensitivity of the copolymer alone is due to the thermal reverse re-

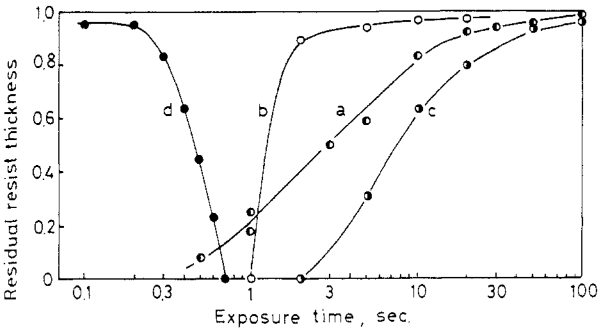


Figure 9. Exposure characteristics of PS-S-12.5: curve a, PS-S-12.5 only; curve b, PS-S-12.5 mixed with CBr_4 (1:1 in weight); curve c, mixture of polystyrene, monomeric spirobenzopyran, and CBr_4 (1:0.5:0.5 in weight); curve d, AZ 1350J.

action back to spiro form of the photogenerated merocyanine during post-exposure baking. The addition of CBr_4 prevents the reverse reaction by generation of a salt or other reaction products with CBr_4.

Monomeric, free spirobenzopyran mixed in polystyrene is also expected to work as a negative resist. Curve c of Figure 9 shows the exposure characteristic curve of the mixture of polystyrene, spirobenzopyran, and CBr_4 (1:0.5:0.5 in weight). The sensitivity and contrast is very poor. This result indicates that incorporation of spirobenzopyran groups to the pendant groups is indispensable to the dissolution rate change by photoirradiation.

Conclusion

The present study has demonstrated that the solubility of polystyrene in cyclohexane can be photocontrolled by incorporating small amounts (~2 mol %) of spirobenzopyran to the pendant groups. The decrease in the solubility is achieved not through interaction among photogenerated merocyanine groups but rather through a decrease of polymer–solvent interaction due to polarity increase of the pendant groups arising from the isomerization of spirobenzopyran. The solubility change resulted in the fractional precipitation. The fractional precipitation was interpreted by the change of molecular weight dependence of critical miscible temperature owing to the configuration of the pendant groups. The copolymer worked as a negative photoresist with high contrast in the presence of CBr_4.

References and Notes

(1) Part 6, Irie, M.; Menju, A.; Hayashi, K. *Nippon Kagaku Kaishi* **1984**, 227.
(2) Irie, M.; Tanaka, H. *Macromolecules* **1983**, *16*, 210.
(3) Irie, M.; Schnabel, W. *Macromolecules* **1985**, *18*, 394.
(4) Irie, M.; Menju, A.; Hayashi, K. *Macromolecules* **1979**, *12*, 1176.
(5) (a) Goldburt, E.; Shvartsman, F.; Fishman, S.; Krongauz, V. *Macromolecules* **1984**, *17*, 1225. (b) Goldburt, E.; Shvartsman, F.; Krongauz, V. *Ibid.* **1984**, *17*, 1876. (c) Krongauz, V. A.; Goldburt, E. S. *Ibid.* **1981**, *14*, 1382.
(6) Kalinsky, Y.; Williams, D. J. *Macromolecules* **1984**, *17*, 292.
(7) Taniguchi, Y.; Hatano, Y.; Shiraishi, H.; Horigome, S.; Nonogaki, S.; Naraoka, K. *Jpn. J. Appl. Phys.* **1979**, *18*, 1143.
(8) Krongauz, V. A.; Goldburt, E. S. *Nature (London)* **1978**, *271*, 43.
(9) (a) McRae, E. G.; Kasha, M. *J. Chem. Phys.* **1958**, *28*, 721. (b) McRae, E. G.; Kasha, M. "Physical Processes in Radiation Biology"; Academic Press: New York, 1964; p 23.
(10) Fox, T. G.; Flory, P. J. *J. Am. Chem. Soc.* **1951**, *73*, 1909, 1915.
(11) Hofer, D. C.; Kaufman, F. B.; Kramer, S. R.; Aviram, A. *Appl. Phys. Lett.* **1980**, *37*, 314.

Quasi-Elastic Light Scattering and Fluorescence Photobleaching Recovery Studies on Poly(lysine) Dynamics

Donald J. Ramsay and Kenneth S. Schmitz*

Department of Chemistry, University of Missouri—Kansas City, Kansas City, Missouri 64110. *Received January 31, 1985*

ABSTRACT: Quasi-elastic light scattering (QELS) and fluorescence photobleaching recovery (FPR) methods were used to study the apparent diffusion coefficient (D_{app}) and the tracer diffusion coefficient (D_{Tr}), respectively, of poly(lysine) of 800 000-dalton molecular weight as a function of [KCl]. The correlation functions from the QELS studies were analyzed by asymptotic analysis and the histogram method with exponential sampling. These analyses indicate that D_{app} splits into two relaxation domains at [KCl] ~ 0.01 M, where the relative values of D_{app} for the two branches differ by over an order of magnitude. In contrast, the added salt profile of D_{Tr} monotonically decreases in value by only a factor of 2 in going from 0.5 M KCl to zero added salt. These observations are discussed in terms of conformational transitions in poly(lysine) and also polyion–small ion and polyion–polyion interactions.

Introduction

Quasi-elastic light scattering (QELS) is a technique that monitors the spontaneous decay of fluctuations in the index of refraction of the medium. It is generally assumed that these fluctuations are due to the decay of concentration gradients of the macromolecules; hence QELS provides a direct measure of the mutual diffusion coefficient (D_m). In the simplest case of center-of-mass translational diffusion in dilute solutions, D_m is proportional to the product of the tracer diffusion coefficient ($D_{Tr} = kT/f$, where kT is the thermal energy and f is the molecular friction factor) and the osmotic compressibility of the solution. Values of D_{Tr} can be obtained from fluorescence photobleaching recovery (FPR) techniques, in which the recovery in fluorescent signal of a bleached region in the solution is monitored. In recent years much attention has been given to solution conditions that induce multiple relaxation modes in the QELS data; hence it is common practice to refer to apparent diffusion coefficients (D_{app}) in the characterization of these decay rates.

The focus of the present study is the diffusion modes of high molecular weight poly(lysine) as inferred from QELS and FPR data. Lin, Lee, and Schurr[1] first reported somewhat bizarre salt concentration (C_s) dependence of D_{app} for this system. After first experiencing an initial rise in value as the concentration of NaBr was decreased to 0.001 M, D_{app} precipitously dropped by over an order of magnitude in value within a narrow range in added salt

0024-9297/85/2218-2422$01.50/0 © 1985 American Chemical Society