Macromolecules **1985,** *18,* 317-321

for their technical assistance. Part of this work was supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science, and Culture.

References and Notes

(1) Part 17 of "Polymerization of Phenylacetylenes". Part 16: Yamagata, M.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2275.

(2) For a review, see: Simionescu, C. I.; Percec, V. *Prog. Polym. Sci.* **1982**, *8*, 133.

(3) For a review, see: Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51.

(4) (a) Sasaki, N.; Masuda, T.; Higashimura, T. *Macromolecules* **1976**, *9*, 664. (b) Masuda, T.; Kawai, H.; Ohtori, T.; Higashimura, T. *Polym. J.* **1979**, *11*, 813. (c) Masuda, T.; Yamagata, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 126. (d) Higashimura, T.; Deng Y.-X.; Masuda, T. *Macromolecules* **1982**, *15*, 234. (e) Masuda, T.; Kuwane, Y.; Higashimura, T. *Polym. J.* **1981**, *13*, 301.

(5) (a) Dändliker, G. *Helv. Chim. Acta* **1969**, *52*, 1482. (b) Masuda, T.; mouri, T.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1152. (c) Masuda, T.; Deng, Y.-X.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2798.

(6) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233.

(7) Masuda, T.; Takahashi, T.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* **1982**, 1297.

(8) Kuwane, Y.; Masuda, T.; Higashimura, T. *Polym. J.* **1980**, *12*, 387.

(9) Masuda, T.; Niki, A.; Isobe, E.; Higashimura, T., submitted for publication in *Macromolecules*.

(10) Shirakawa, H.; Sasaki, T.; Ikeda, S. *Chem. Lett.* **1978**, 1113.

(11) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(12) E.g.: Jackson, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2935.

(13) Masuda, T.; Tang, B.-Z.; Higashimura, T.; Yamaoka, H., submitted for publication in *Macromolecules*.

Poly[*p*-(formyloxy)styrene]: Synthesis and Radiation-Induced Decarbonylation

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ABSTRACT: Poly[*p*-(formyloxy)styrene] is prepared by chemical modification of poly(*p*-hydroxystyrene) or free-radical-initiated polymerization of the corresponding monomer. Unlike poly(*p*-acetoxystyrene), which undergoes a partial photochemical Fries rearrangement, poly[*p*-(formyloxy)styrene] decarbonylates smoothly when exposed to UV irradiation in solution or in the solid state. The difference in reactivity between the two acylated polymers is likely due to the lower stability of the formyl radical which is formed in the first stage of the photo-Fries reaction. In addition, while uniform irradiation of a 1-μm film of poly(*p*-acetoxystyrene) is impossible because of the formation of a strongly absorbing and UV stabilizing polymer at the surface of the exposed film, poly[*p*-(formyloxy)styrene] can be used in microlithographic processes to produce high-resolution relief images. The images can be developed with positive or negative tone by differential dissolution of the exposed and unexposed areas of the polymer film by using solvents of appropriate polarities.

Introduction

The photo-Fries rearrangement of aromatic esters and amides which was first reported by Anderson and Reese[1] has been tested with a number of polymeric materials such as aromatic polyesters[2-4] and polyamides.[5] Early interest in this photoinduced rearrangement was mainly due to its applicability to the problem of polymer stabilization. Thus, Cohen et al.[4] have shown that the rearrangement of fully aromatic polyesters produces polymers containing *o*-hydroxy-substituted units which confer great UV stability to the rearranged polymer. The general photostabilizing action of *o*-hydroxy aromatic compounds has been reviewed recently by Allen[6] and by Ranby and Rabek.[7] Similarly, much work on polymers containing aromatic ester or amide pendant groups[3,8] has confirmed that the photo-Fries rearrangement of these polymers is accompanied by the generation of photostabilizing groups. Following a thorough study of the photo-Fries reaction, Guillet et al. concluded that the enhanced stability of the rearranged products was due in part to their high extinction coefficients and in part to their ability to dissipate the absorbed energy through nonphotochemical pathways.[9]

Our interest[10,11] in polymeric imaging systems for application in microelectronics has led us to consider the applicability of the photo-Fries reaction of polymers containing aromatic ester or amido groups. For example, it is expected that the light-induced Fries rearrangement of poly(*p*-acetoxystyrene) will yield a rearranged polymer containing pendant phenolic groups. Such rearrangement would afford a basis for development of an image from a thin film of the polymer as the unexposed and exposed areas of the polymer would have greatly dissimilar polarities and could thus be resolved by differential dissolution in appropriate solvent systems.

Results and Discussion

Our initial study was focused on the photo-Fries rearrangement of poly(*p*-acetoxystyrene) (I), which can be prepared by free-radical polymerization of the corresponding monomer.[12] Progress of the photoinduced rearrangement was monitored by Fourier transform infrared or by UV spectroscopy using 1-μm films of the polymer cast on sodium chloride or quartz disks. As the starting polymer absorbs weakly in the deep UV near 270 nm, a high-pressure mercury–xenon lamp with quartz optics was used for the irradiation experiments. The results of these experiments show that the photo-Fries rearrangement of poly(*p*-acetoxystyrene) does occur but only with low efficiency.

The infrared spectrum of the polymer changes as exposure dose is increased with the appearance of a new carbonyl band at 1642 cm^{-1} and a weak hydroxyl band centered at 3483 cm^{-1}; the appearance of these two bands, which correspond to the newly formed *o*-hydroxy ketone

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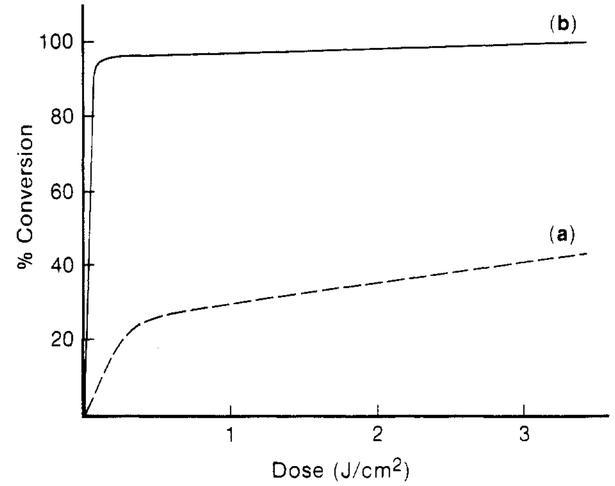
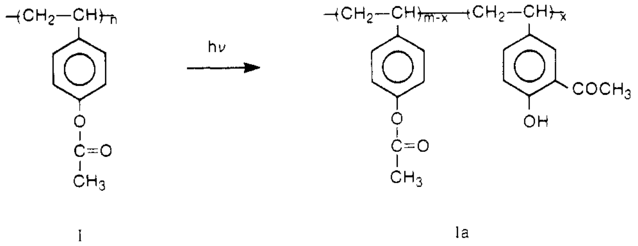


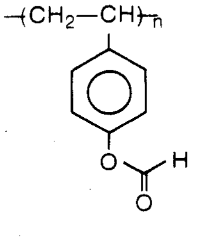
Figure 1. Percent photoconversion in the photo-Fries reaction of (a) poly(p-acetoxystyrene) and (b) poly[p-(formyloxy)styrene].

Scheme I



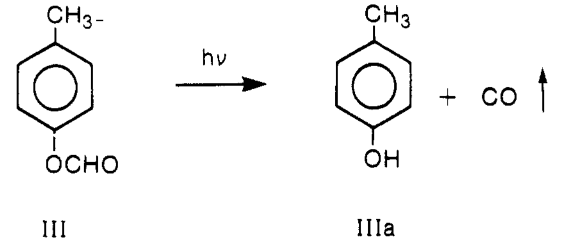
units in the exposed polymer (Ia, Scheme I), is also accompanied by a decrease in the intensity of the starting ester band at 1761 cm^{-1}. Figure 1a shows the percentage of rearranged units which are formed when poly(p-acetoxystyrene) is subjected to increasing exposure doses of UV radiation. Clearly the reaction becomes very sluggish as conversion increases and essentially stops when 40–50% of the starting polymer's repeating units have been converted. This finding, which is not totally unexpected in view of the photostabilizing effect of the rearranged units Ia, reduces greatly the potential of poly(p-acetoxystyrene) as a resist material since incomplete conversion of the exposed areas of films of the polymer is likely to cause problems in the image development step.

Thus, it is desirable to replace polymer I with another polymer which would have a lesser tendency to produce photostabilizing rearranged units upon exposure to UV light. A survey of the literature dealing with the photo-Fries rearrangement of esters suggests that formate esters may be more suitable than their acetate counterparts. Horspool and Pauson[13] have shown that irradiation of (formyloxy)benzene affords phenol as the major product. Since phenol absorbs much less in the deep UV than typical rearranged products such as o-hydroxyphenones, it is expected that poly[p-(formyloxy)styrene] (II) might prove superior to I as a polymeric imaging system. Model reactions with p-cresyl formate (III) confirm that irradiation results in the predominant formation of p-cresol (IIIa) with only a small amount of unreacted starting material remaining and no detectable formation of the ortho rearranged product IIIb (Scheme II). Poly[p-(formyloxy)styrene] was prepared for the first time both by chemical modification of poly(p-hydroxystyrene)[10] and by radical-initiated polymerization of the previously unreported monomer. The functionalization of poly(p-hydroxystyrene) was accomplished by using a mixture of formic and acetic anhydride as formylating agent[14] (Scheme III). The reaction, which is catalyzed by pyridine, is slow and usually incomplete, requiring several days to reach 98% conversion. The monomer was prepared from p-hydroxybenzaldehyde according to Scheme IV. Again the formylation reaction was accomplished via the mixed anhydride.

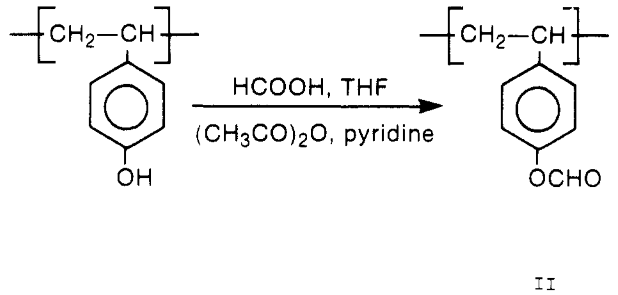


II

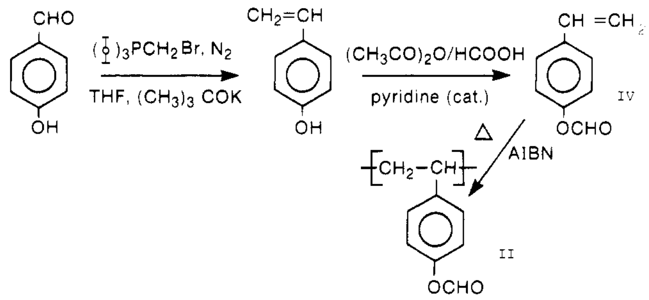
Scheme II



Scheme III



Scheme IV



The polymer II which is obtained shows a characteristic twin carbonyl band at 1738–1761 cm^{-1} in its infrared spectrum. This is due not to a competing acetylation reaction, as essentially no acetate is formed during the formylation, but rather to the presence of both cis and trans conformations of the formate groups in the polymer. Such conformations of formates have been observed previously for other formates[15] as well as for carboxylic acids and amides.[16,17] The carbonyl stretching absorption for the cis conformer occurs at higher frequency than for the trans conformer (1761 vs. 1738 cm^{-1}) since a higher energy is required to excite the molecule when the two dipoles are parallel.

Irradiation of II in solution or in the solid state affords the same results. In both cases, infrared monitoring of the reaction shows that it is accompanied by extensive decarbonylation as evidenced by the sharp decrease in in-

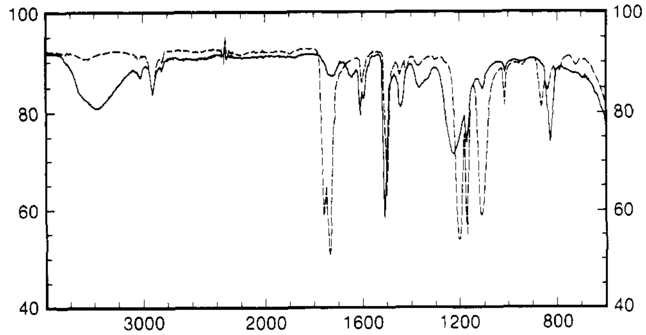
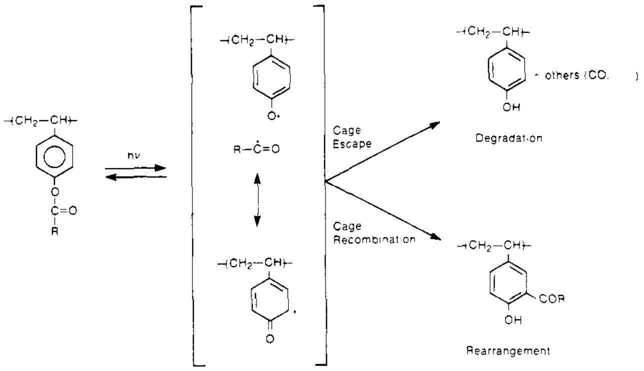


Figure 2. Infrared spectrum of poly[p-(formyloxy)styrene] before (---) and after (—) exposure to 100 mJ/cm^2.

tensity of the carbonyl bands of II upon exposure. It is interesting to note that the intensity of the carbonyl stretching band assigned to the cis conformer (1761 cm^{-1}) decreases at a faster rate upon irradiation than that of the trans conformer. This suggests that the cis conformer is the least stable to UV irradiation and confirms earlier studies on the nonphotochemical stability of the conformers of phenyl formate.[15]

Exposure of 1 μm thick films of II shows that over 90% decarbonylation is achieved with radiation doses of less than 100 mJ/cm^2 (Figure 2). Only a very small amount of starting material remains unchanged while careful examination of the infrared spectrum of the exposed polymer shows that a very small amount of ortho rearranged product is also formed as evidenced by the appearance of a very weak carbonyl band at 1641 cm^{-1} which corresponds to the hydrogen-bonded carbonyl group of the rearranged o-hydroxyaldehyde. Overall better than 94% conversion to poly(p-hydroxystyrene) is obtained with an exposure of 100 mJ/cm^2. This result is in sharp contrast with that obtained in the photo-Fries reaction of I which undergoes partial rearrangement to the corresponding poly(3-acetyl-4-hydroxystyrene) with little or no concurrent degradation while photodegradation occurs almost exclusively with II. The mechanism of the photo-Fries reaction of aromatic esters has been studied extensively and two basic mechanisms have been proposed. The first one involves a concerted mechanism in which the rearrangement proceeds through a bicyclic diradical intermediate,[18] while the second suggests that homolytic cleavage of the ester linkage produces a radical pair which can undergo recombination,[19] perhaps in a solvent cage. In this latter mechanism, the recombination can lead to either the starting ester or a rearranged o- or p-hydroxy ketone as shown in Scheme V. Although slightly modified versions of the concerted mechanism have been proposed,[20,21] there is much experimental evidence to support the cage recombination mechanism.[22,23] As the Fries degradation is observed with polymer II even in a strongly caging solvent such as acetonitrile, the results of the irradiation of poly(p-acetoxystyrene) and poly[p-(formyloxy)styrene] suggest that decomposition of the unstable formyl radical occurs rapidly within the solvent cage, thereby preventing recombination of the radical pair which would afford either starting or rearranged products. This proposal agrees with the observation[13] that a larger amount of carbon monoxide is formed when phenyl formate is irradiated than when other esters of phenol are used.

Scheme V



The photodegradation of poly[p-(formyloxy)styrene] can also be monitored by UV spectrometry as the phenolic photoproduct absorbs slightly more in the 250–300-nm range than its unexposed precursor. The change in absorbance is however much smaller than that which is observed during irradiation of poly(p-acetoxystyrene) and the photodegradation can proceed rapidly to near completion.

Lithographic testing[25] of 1 μm thick films of poly[p-(formyloxy)styrene] cast on silicon wafers confirmed that the polymer can be used to generate relief images of positive or negative tone depending on the development conditions. When selected areas of polymer II are exposed to UV radiation, the decarbonylation reaction which occurs transforms the starting lipophilic polymer into base-soluble poly(p-hydroxystyrene). The great difference in solubility which exists between the exposed (phenolic) and unexposed (ester) areas of the polymer film can be used advantageously to develop a positive image by dissolution of the exposed areas, or of a negative image by selective removal of the unexposed material. In practice, well-resolved images with 1.25-μm minimum features can be obtained with exposure doses as low as 70 mJ/cm^2. Figure 3 shows a positive and a negative image which were obtained from the same silicon wafer coated with a 1 μm thick film or poly[p-(formyloxy)styrene]; the wafer was cut in two after exposure and one-half was imaged by dissolving the exposed areas of in a 10:1:1 mixture of isopropyl alcohol–concentrated ammonium hydroxide–water mixture to yield a positive image while a negative image of similar quality was obtained by dissolving the unexposed areas of the film in 1:1 dichloromethane–hexane mixture.

In contrast, thin films of poly(p-acetoxystyrene) cannot be used in a similar microlithographic process as the polarity difference between the partially exposed (ca. 40%) and the unexposed polymer was insufficient to afford a fully developed image. An additional problem with polymers such as poly(p-acetoxystyrene) is that as the photo-Fries rearrangement occurs first near the surface of the film, the ortho-rearranged product which is formed absorbs the radiation and prevents it from reaching the lower layers of the film, thus greatly decreasing image resolution; this problem is of major importance even with films as thin as 1 μm.

Conclusion

While other polymers containing phenolic moieties undergo a partial Fries rearrangement when exposed to UV radiation, poly[p-(formyloxy)styrene] is decarboxylated almost quantitatively to poly(p-hydroxystyrene). This behavior, which is observed both in the solid state and in solution, can be attributed to the lack of stability of the formyl radical which is formed upon UV exposure. This radical decomposes rather than undergo the recombination reaction which is characteristic of other acyl radicals in the Fries reaction. As irradiation of poly[p-(formyloxy)styrene] in the deep UV results in the formation of the much polar poly(p-hydroxystyrene), imaging of thin films of the polymer is possible and leads to a latent image which can be developed at will in the positive or the negative tone

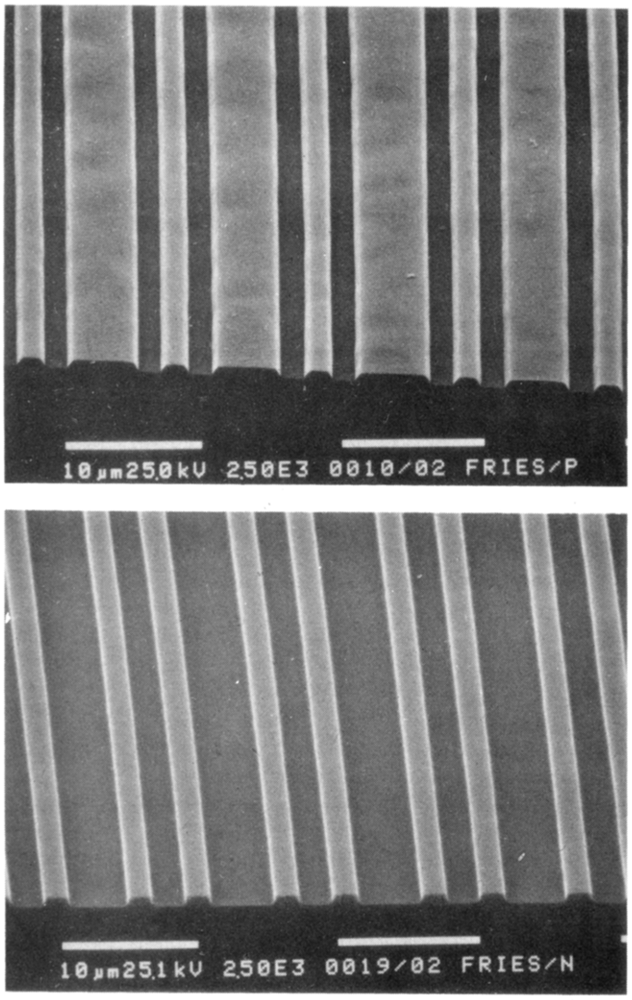


Figure 3. Positive (top) and negative (bottom) tone images in poly[*p*-(formyloxy)styrene]. The images were projection printed in the deep UV.

depending on the polarity of the developing solvent. This versatility of poly[*p*-(formyloxy)styrene] coupled to its sensitivity and resolution, which are similar to those of many current novolac-based resists,[25] confirm its usefulness as a positive or negative photoresist material. Of particular significance is the fact that the new resist can be used in the deep UV, an area of the spectrum where few other materials can be used.

Experimental Section

Spectrometric monitoring of the reactions was carried out with a Nicolet MX-1 Fourier transform infrared spectrometer and a Hewlett-Packard UV–visible spectrometer. All infrared spectra were recorded on thin films of polymer cast on sodium chloride disks, while UV spectra were recorded from films cast on quartz disks. A Headway research spin coater was used to prepare the films of polymer on silicon, sodium chloride, or quartz substrates. Film thickness measurements were made with a Talystep or Sigmascan profilometer. Solid-state UV exposures were performed by using an Optical Associates, Inc., Model 30 deep-UV illuminator with quartz optics. Flux measurements were performed on an O.A.I. Model 354 exposure monitor with 260-nm probe. Photochemical exposures in solution were carried out by using an Ace glass reactor with quartz lamp housing and a 500-W Hanovia lamp. NMR spectra were measured on Varian EM360 or CFT80 spectrometers; chemical shifts were measured from deuterated chloroform solutions and are reported as δ values in ppm from Me_4Si. All chemicals used were reagent grade unless otherwise specified.

Preparation of *p*-Hydroxystyrene. A mixture of 50 g of methyltriphenylphosphonium bromide in 100 mL of dry THF is treated with 33.6 g of potassium *tert*-butoxide and 17.1 g of *p*-hydroxybenzaldehyde is added under inert atmosphere while keeping the stirred reaction mixture under 25 °C. The mixture is stirred for 1 h and then poured into ice water and the oily material which forms is extracted with ethyl acetate. After workup and purification by preparative HPLC 14.2 of pure *p*-hydroxystyrene (85%) is obtained as a solid: mp 72–73 °C; mass spectrum, m/e 120 (M^+, base peak); ^1H NMR δ 5.16, 5.62, and 6.66 (AMX pattern for vinyl protons, $J_{AM} = 0.75$ Hz, J_{AX} 11 Hz, and J_{MX} 18 Hz), 6.86 (2 H, d, aromatic, $J = 8$ Hz), 7.35 (2 H, d, aromatic, $J = 8$ Hz), 5.10 (1 H, s, OH); IR 3383, 1629 cm^{-1} (OH and C=C, respectively).

Preparation of *p*-(Formyloxy)styrene. A formylating mixture consisting of 9.0 g of formic acid and 19.9 g of acetic anhydride is prepared by mixing the two reagents slowly while keeping the temperature below 45 °C according to the procedure of Stevens and Van Es.[14] After cooling to room temperature the formylation reagent is treated with a mixture of 0.35 g of pyridine and 10.9 g of *p*-hydroxystyrene and the solution is stirred for 3 days. The solution is then concentrated in vacuo, leaving a yellowish residue which is purified by fractional distillation (bp 83 °C at 3 mmHz) to yield 11.0 g (82%) of *p*-(formyloxy)styrene: mass spectrum, m/e 148 (M^+), 120 (base peak), 29 (HCO^+), and 27 ($CH_2{=}CH^+$); IR 1763 and 1739 (formate ester), 1631 (C=C) cm^{-1}; ^1H NMR δ 5.17, 5.63, 6.55 (AMX pattern for vinyl protons, $J_{AM} = 1.0$ Hz, $J_{AX} = 10.6$ Hz, and $J_{MX} = 17$ Hz), 6.98 (2 H, d, aromatic), 7.35 (2 H, d, aromatic), 8.16 (1 H, OCHO).

Polymerization of *p*-(Formyloxy)styrene. A solution of 0.06 g of AIBN in 6.1 g of *p*-(formyloxy)styrene is heated to 80 °C overnight under inert atmosphere. The resulting polymer is dissolved in THF and precipitated in petroleum ether. After washing and drying 4.85 g of poly[*p*-(formyloxy)styrene] is obtained. The polymer has M_n 11 000 and M_w 16 500 (GPC): IR 1761 and 1738 (C=O), 1205, 1169, and 1107 (C—O) cm^{-1}; ^1H NMR δ 0.91–2.24 (3 H, m, CH_2–CH), 6.23–7.24 (4 H, m, aromatic), 8.22 (1 H, s, O–CHO).

Formylation of Poly(*p*-hydroxystyrene). The formylating agent is prepared by reaction of 3.87 g of formic acid with 8.54 g of acetic anhydride while keeping the temperature of the mixture below 45 °C. A solution of 4.5 g of poly(*p*-hydroxystyrene)[10] in 30 mL of THF containing 0.1 g of pyridine is then added to the stirred formylating agent and the mixture is stirred for 3 days at room temperature. After precipitation in water, the polymer is washed and dried to afford 4.99 g of poly[*p*-(formyloxy)styrene]. Spectroscopic analysis of the polymer confirms that a very small amount of unreacted *p*-hydroxystyrene units remain unchanged in the polymer.

Preparation of Poly(*p*-acetoxystyrene). The *p*-acetoxystyrene monomer is prepared from *p*-hydroxyacetophenone by the procedure of Corson et al. Polymerization is carried out by using a solution of 9.95 g of the monomer in 60 mL of toluene containing 0.1 g of AIBN by heating the stirred mixture to 70–75 °C under inert atmosphere for 24 h. The polymer precipitated in methanol had M_n 11 700 and M_w 20 600 by GPC and M_n 18 500 by osmometry: IR 1761 (C=O), 1218, 1206, and 1017 (C—O), 846 (para-disubstituted aromatic), cm^{-1}; ^1H NMR δ 1.03–1.97 (3 H, m, CH_2–CH), 2.19 (3 H, s, CH_3), 6.23–7.13 (4 H, M, aromatic).

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References and Notes

(1) Anderson, J. C.; Reese, C. B. *Proc. Chem. Soc.* **1960**, 217.
(2) Maerov, S. B. *J. Polym. Sci.* **1965**, *A*-3, 487.
(3) Bellus, D.; Slama, P.; Hrdovic, P.; Manasek, Z.; Durisinova, L. *J. Polym. Sci.* **1969**, *22*, 629.
(4) Cohen, S. M.; Young, R. H.; Markhart, A. H. *J. Polym. Sci., Part A-1* **1971**, *9*, 3263.
(5) Carlsson, D. J.; Gan, L. H.; Wiles, D. M. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2353.
(6) Allen, N. S. *Polym. Photochem.* **1983**, *3*, 167.
(7) Ranby, B.; Rabek, J. F. "Photodegradation, Photooxidation, and Photostabilization of Polymers"; Wiley: New York, 1975.
(8) Li, S. K. L.; Guillet, J. E. *Macromolecules* **1977**, *10*, 840.
(9) Guillet, J. E.; Merle-Aubry, L.; Holden, D. A.; Merle, Y. *Macromolecules* **1980**, *13*, 1138.

Macromolecules **1985,** *18,* 321-327 **321**

(10) Fréchet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1983,** *24,* 995.
(11) Ito, H.; Willson, C. G.; Fréchet, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* **1983,** *16,* 510.
(12) Danusso, F.; Ferruti, P.; Gazzaniga-Marabelli, C. *Chim. Ind. (Milan)* **1965,** *47,* 493.
(13) Horspool, V. M.; Pauson, P. L. *J. Chem. Soc.* **1965,** 5162.
(14) Stevens, W.; Van Es, A. *Recl. Trav. Chim. Pays-Bas* **1965,** *84,* 1247; **1964,** *83,* 1294.
(15) Oki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1970,** *43,* 2558.
(16) Oki, M.; Hirota, M. *Bull. Chem. Soc. Jpn.* **1960,** *33,* 119; **1961,** *34,* 374.
(17) Kessler, H.; Rieker, A, *Ann. Chem.* **1967,** *708,* 57.
(18) Anderson, J. C.; Reese, C. B. *J. Chem. Soc.* **1963,** 1781.
(19) Kobsa, H. *J. Org. Chem.* **1962,** *27,* 2293.
(20) Bellus, D. *Adv. Photochem.* **1971,** *8,* 109.
(21) Sander, M. R.; Hedaya, E.; Trecker, D. J. *J. Am. Chem. Soc.* **1967,** *89,* 5725.
(22) Meyer, J. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1972,** *94,* 2219.
(23) Kalmus, C. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1974,** *96,* 449.
(24) Corson, B. B.; Heintzelman, W. J.; Schwartzmann, L. H.; Tiefenthal, H. E.; Lokken, R. J.; Nickels, J. E.; Atwood, G. R.; Pavlik, F. J. *J. Org. Chem.* **1958,** *23,* 544.
(25) Thompson, L. F.; Willson, C. G.; Bowden, M. J. "Introduction to Microlithography"; American Chemical Society: Washington, DC, 1983; *ACS Symp Ser.* No. 219.

Photoresponsive Polyquinolines

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ABSTRACT: Photoresponsive polyquinolines containing isomerizable stilbene units were synthesized by polymerization reactions utilizing 4,4′-diacetylstilbene (**2**) as the bis(ketomethylene) monomer and 4,4′-diamino-3,3′-dibenzoylstilbene (**3**) as the bis(amino ketone) monomer. The diacetylstilbene monomer (**2**) was polymerized with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 3,3′-dibenzoylbenzidine, and **3**. Monomer **3** also was polymerized with 4,4′-diacetyldiphenyl ether and 4,4′-diacetylbiphenyl. These polymers exhibited photoviscosity effects in dilute solution, ranging from a 2% to a 23% change in viscosity during irradiation. Photomechanical measurements showed that films of the polymer contracted by as much as 5% when irradiated above T_g. A smaller contraction was observed upon irradiation below T_g. In addition, the polymer obtained from **2** and 3,3′-dibenzoylbenzidine produced an anisotropic solution (10% (w/w) in *m*-cresol/di-*m*-cresyl phosphate).

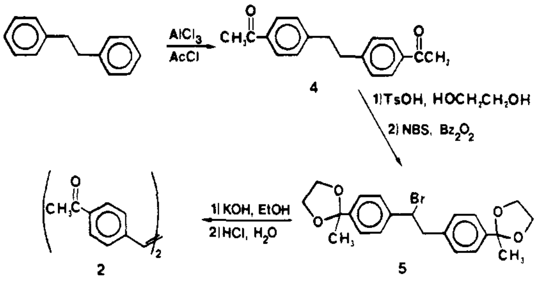
Introduction

Since the concept of photoresponsive polymers was first suggested in 1967,[1] a variety of photoresponsive polymers have been studied.[2] The work was concentrated primarily on polymers incorporating azobenzene or spirobenzopyran residues as the photoresponsive units. While the azobenzene undergoes simple *E* to *Z* isomerization, the spirobenzopyran undergoes a reversible photoinduced rearrangement to a merocyanine. These chromophores have been incorporated into polymers in the main chain,[3,4] as pendant groups,[5-7] as cross-links,[6] or simply as additives.[6,8] Previous research has focused on flexible and semirigid polymers such as polyamides,[3,8] polyurethanes,[4,9] polyacrylates,[6,7] and polystyrenes.[5]

Numerous physical properties of photoresponsive polymers have been shown to be altered when the chromophoric units are isomerized. These properties include dilute solution viscosity,[3,7] conductivity,[3] pH,[3] and solubility.[5] In addition, polymer chain mobility has been probed by the trans–cis isomerization of azobenzene units in the polymer chain.[4,9-11]

A study of the photochemical behavior of 4,4′-disubstituted stilbenes indicated that they isomerized readily.[12] There are two examples in which stilbene has been incorporated into a polymer main chain. The quantum efficiency for stilbene isomerization in copolyamides has been measured.[13] The viscosity of a polyaramide containing stilbene units contained in the diamine monomer showed a decrease on irradiation and slowly recovered in the dark.[14] Unexpectedly, the same polymer in bulk relaxed instead of contracting on irradiation.

Scheme I
Synthesis of 4,4′-Diacetylstilbene (2)



Although rigid rod polyquinolines demonstrate excellent thermal stability, high phase transition temperatures, and a high degree of crystallinity, they are relatively insoluble, even in acidic solvents such as sulfuric acid and trifluoromethanesulfonic acid.[15] This research was undertaken, therefore, to improve the processability of rigid rod polyquinolines by incorporating photoisomerizable (*E*)-stilbene units in the main chain. Irradiation of these polymers was expected to effect an *E* to *Z* isomerization converting the rigid rod polymer to a nonlinear one, thereby aiding in its dissolution. Thermal relaxation of the *Z* isomer could again generate the rigid rod after processing.

Results and Discussion

Stilbene Monomers. Before proceeding with large-scale preparations of the stilbene monomers, we prepared a model compound (**1**) from 4,4′-diacetylstilbene (**2**) and *o*-aminobenzophenone. Synthesis of **1** under the same conditions as the polymerizations indicated that the stilbene monomers could be successfully polymerized without decomposition. Because of the mild electron-withdrawing character of the quinoline ring, isomerization of the stilbene unit in the polymer should proceed smoothly, re-

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