(33) Zutty, N. L.; Welch, F. J. *J. Polym. Sci., Part A* **1963**, *1*, 2289-2297.
(34) Zutty, N. L.; Welch, F. J. U.S. Patent 3,321,417, 1967.
(35) Burnett, G. M.; Haldon, R. A.; Hay, J. N. *Eur. Polym. J.* **1968**, *4*, 83-92.
(36) Rasmussen, R. S.; Brattain, R. R. *J. Am. Chem. Soc.* **1949**, *71*, 1073-1079.
(37) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th Ed.; Wiley: New York, 1981; pp 95-180.

GC/MS Study of the Thermolysis and Acidolysis of Poly(*t*-BOC-α-methylstyrene), Poly(*t*-BOC-styrene), and Poly(*t*-BOC-styrene sulfone)

F. M. Houlihan,* E. Reichmanis,* R. G. Tarascon, G. N. Taylor, M. Y. Hellman,† and L. F. Thompson

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received November 16, 1988; Revised Manuscript Received January 19, 1989*

ABSTRACT: The thermolysis and acidolysis of three polymers, poly(4-((*tert*-butoxycarbonyl)oxy)-α-methylstyrene) [poly(*t*-BOC-α-methylstyrene)], poly(4-((*tert*-butoxycarbonyl)oxy)styrene) [poly(*t*-BOC-styrene], and poly(4-((*tert*-butoxycarbonyl)oxy)styrene sulfone) [poly(*t*-BOC-styrene sulfone)], were studied by gas chromatography/mass spectroscopy. The acidolysis reaction was investigated with both thermally and photochemically generated acid. The photogenerators of acid considered in this study were triphenylsulfonium hexafluoroarsenate and 2,6-dinitrobenzyl tosylate. The thermal generator of tosic acid was 2-nitrobenzyl tosylate. It was found that the presence of acid caused the expected deprotection of the phenol functionality with liberation of CO_2 and isobutene in all three polymer systems. However, in the case of poly(*t*-BOC-α-methylstyrene), a depolymerization reaction was also observed with liberation of 4-hydroxy-α-methylstyrene. The extent of depolymerization was found to be as high as 20% in some cases, and a secondary product, 5-hydroxy-1,1,3,3-tetramethylindan, was observed.

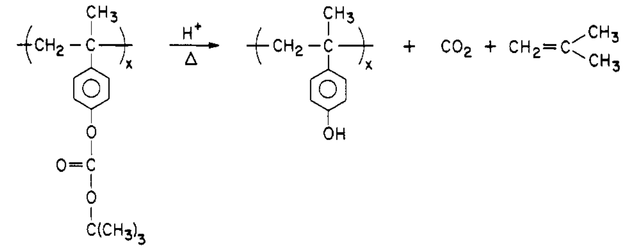
Introduction

Poly(*t*-BOC-styrene) and poly(*t*-BOC-α-methylstyrene) have been reported as forming sensitive deep UV resists when used in combination with materials that photogenerate acid.[1,2] The sensitivity of these resists is derived from the phenomenon of chemical amplification where photochemically generated acid causes the catalytic removal of the *t*-BOC group (Scheme I). This process has an effective quantum yield of reaction for the resist that far exceeds that of the acid photogenerator. We have been studying these two polymers along with a novel material, poly(*t*-BOC-styrene sulfone), for application with a new, nonionic deep UV photogenerator of acid, 2,6-dinitrobenzyl tosylate (Scheme II) that we have devised.[2] Here, we examine the chemistry of these resists using gas chromatography/mass spectroscopy (GC/MS) analysis and gel permeation chromatography (GPC). Thermolysis was carried out in both the absence and presence of acid. Triphenylsulfonium hexafluoroarsenate and 2,6-dinitrobenzyl tosylate were used to photochemically generate acid, while 2-nitrobenzyl tosylate was used to evaluate the effect of thermally generated tosic acid. Scheme III depicts the mechanism of thermal generation of tosic acid from 2-nitrobenzyl tosylate.

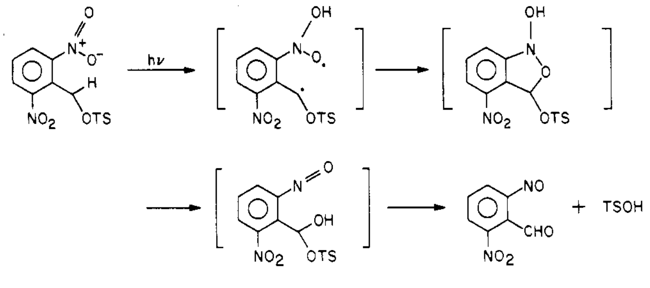
Experimental Section

Materials. The nitrobenzyl tosylates[2] and triphenylsulfonium hexafluoroarsenate[3] were prepared as described in the literature. The monomers *t*-BOC-α-methylstyrene and *t*-BOC-styrene were supplied by H & S Chemicals Inc. and distilled under vacuum prior to use. Poly(*t*-BOC-α-methylstyrene) and poly(*t*-BOC-styrene) were prepared by procedures adapted from the literature.[1] The copolymerization of *t*-BOC-styrene and sulfur dioxide is reported elsewhere.[4] Nuclear magnetic resonance spectra of all products were obtained on a JEOL JNM-FX90Q Fourier transform spectrometer.

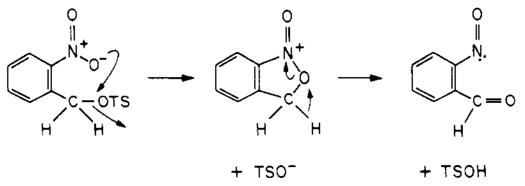
Scheme I



Scheme II



Scheme III



GC/MS Studies. GC/MS experiments were done using an HP5995c mass spectrometer equipped with a cross-linked methyl silicone column (0.2-mm diameter, 12-m length) and helium carrier gas at a flow rate of 0.5 mL/min. A split interface was used with

---

† Currently at Hoechst-Celanese Central Research, Summit, NJ.

0024-9297/89/2222-2999$01.50/0

a split ratio of 1/100. The column temperature was held at −10 °C for 2 min followed by a rapid ramp at (30 °C/min) to 250 °C. Samples of polymer were heated on a Chemical Data Systems platinum ribbon probe. The probe was calibrated for the lower temperature range (80–100 °C) by using an Omega Engineering Inc. microprocessor thermometer equipped with a precision fine wire (5-mil diameter) chromel/alumel thermocouple; for the higher temperature range (300–1000 °C) the calibration chart supplied by Chemical Data Systems was used. Polymers were dissolved in cyclohexanone or xylene (1 wt %). To these solutions were added, as appropriate, 2-nitrobenzyl tosylate, tosic acid hydrate, 2,6-dinitrobenzyl tosylate, or triphenyl sulfonium hexafluoroarsenate (5 wt % relative to the polymer). Polymer films were cast onto the platinum ribbon by using 10 μL of solution, and the probe was then heated to either 80 °C (2-nitrobenzyl tosylate samples) or 120 °C (all other samples). In the case of the samples containing 2-nitrobenzyl tosylate, GC/MS spectra were taken of the volatile products evolving from cast and baked films that were heated at 130 °C for 2 min. In the case of the samples containing 2,6-dinitrobenzyl tosylate or triphenylsulfonium hexafluoroarsenate, GC/MS spectra were taken of the volatile products evolving from cast and baked films that were irradiated at 248 nm with a dose of 195 mJ/cm^2, by using a Suss MA56A contact aligner equipped with a Lambda Physik excimer laser and then heated to 120 °C. In all cases, spectra were taken of the volatile material given off during the pyrolysis of remaining material at 725 °C for 2 min. The percent depolymerization of polymer during the initial heating period is defined as the ratio of the amount of the products given off during the postirradiation bake at 120 °C (or a simple bake in the case of the samples treated with 2-nitrobenzyl tosylate) and the total amount of products given off during both this bake and the final pyrolysis. The depolymerization products were isolated to calibrate the GC/MS results and precisely calculate the percent depolymerization. Polymer samples of 1.0–1.5 g were either thermolyzed at temperatures of 200–300 °C or, in the case of samples containing 5% tosic acid hydrate, heated at temperatures of 100–300 °C. The volatile compounds were collected on a liquid nitrogen cooled coldfinger. Separation of the mixture arising from acid-catalyzed decomposition was accomplished by repeated thick-plate chromatography (silica gel, Merk 60F254) using an ethyl acetate–hexane (1:9) solvent mixture as the eluent.

GPC Studies. GPC analyses were performed with a Waters Model 244 chromatograph using seven Microstyragel columns having porosities of 10^6, 10^5, 10^4, 10^3, 5×10^2, 10^2, and 10^2 Å. Both a differential refractive index detector and UV detector (254 nm) were used. Tetrahydrofuran (THF) was the eluant with a flow rate of 2 mL/min. A benzene internal standard was employed to correct for flow variations and for normalization of the integrated peak areas. The column set was calibrated by using nearly monodisperse polystyrene standards, and all molecular weights are reported in units of polystyrene-equivalent molecular weight.

Samples for analysis were prepared by spin coating 4-in. diameter Si wafers with cyclohexanone solutions of 2,6-dinitrobenzyl tosylate and poly(*t*-BOC-α-methylstyrene) or poly(*t*-BOC-styrene) at 4000 rpm. The wafers were prebaked at 90 °C for 15 min in a convection oven. The samples were analyzed after (a) no further treatment, (b) exposure to 248-nm light (500 mJ/cm^2), and (c) exposure and heating at 120 °C for 30 min in a convection oven. The the film on each wafer was dissolved with 5 mL of THF, and a 1-mL aliquot of 0.1 vol % benzene in THF was added. Finally, the solution was diluted to 10 mL with THF. This solution (100 μL) was injected onto the GPC for analysis.

Results

Thermolysis of pure poly(*t*-BOC-α-methylstyrene), poly(*t*-BOC-styrene), and poly(*t*-BOC-styrene sulfone) films was carried out at 130 °C, and no volatile products, other than those from the solvent, were detected. Pyrolysis at 725 °C gave rise both to deprotection of the BOC group (isobutene, carbon dioxide) and to depolymerization giving the respective monomers sulfur dioxide and 4-hydroxystyrene or 4-hydroxy-α-methylstyrene. The identification of isobutene, CO$_2$, and SO$_2$ utilized a computerized search of an NBS mass spectral library. The compounds 4-hydroxystyrene (retention time (rt) = 7.8 min) and 4-hydroxy-α-methylstyrene (rt = 8.2 min) were identified on the basis of their mass spectra (Figure 1A,B), which were consistent with those reported in the literature for these materials.[5,6] In the case of 4-hydroxy-α-methylstyrene, an authentic sample was obtained upon pyrolysis of gram quantities of poly(*t*-BOC-α-methylstyrene). The spectral characteristics of this material agreed with the above assignment.

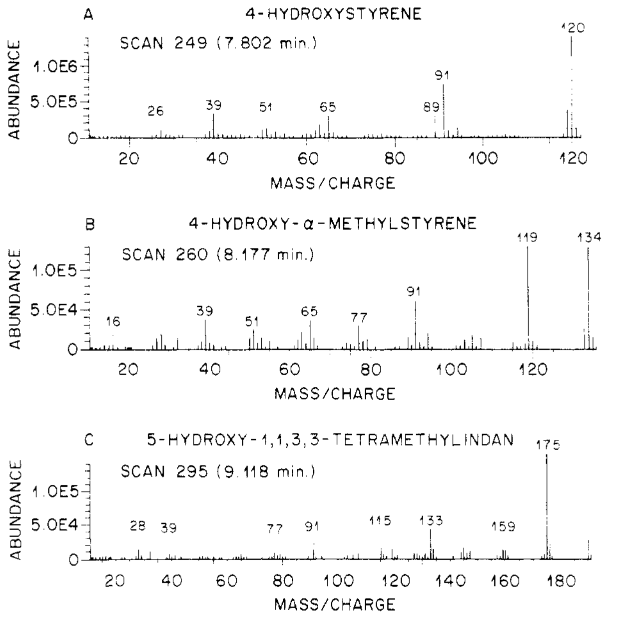


Figure 1. MS traces of the pyrolysis products (A) 4-hydroxystyrene, (B) 4-hydroxy-α-methylstyrene, and (C) 5-hydroxy-1,1,3,3-tetramethylindan.

Thermally Initiated Depolymerizations. The effect of acid on the thermolysis of the styrene polymers was evaluated by using both thermal and photochemical acid generators. The former was investigated by using 2-nitrobenzyl tosylate as the acid precursor. As reported previously,[2] this ester undergoes thermal decomposition at 100 °C to yield anhydrous tosic acid.

When films of poly(*t*-BOC-styrene) and the copolymer of sulfur dioxide and *t*-BOC-styrene containing 5 wt % 2-nitrobenzyl tosylate were heated to 130 °C, only products arising from the decomposition of the *t*-BOC group (carbon dioxide, isobutene, oligomers of isobutene) were detected. Films cast from the third polymer, poly(*t*-BOC-α-methylstyrene), gave products arising not only from the deprotection process but also from a depolymerization reaction. Two products of depolymerization were observed, the expected 4-hydroxy-α-methylstyrene and an unknown compound having a retention time of 9.1 min. The mass spectrum of this material is shown in Figure 1C. A similar depolymerization was observed when tosic acid hydrate was used as the source of acid, indicating that the process is acid initiated. Authentic samples of this unknown compound were obtained upon tosic acid hydrate catalyzed depolymerization of gram quantities of the polymer. From C-13 and H-1 NMR along with the mass spectral data, this material was identified as 5-hydroxy-1,1,3,3-tetramethylindan [H-1 NMR δ 6.95 (d, J = 8.4 Hz, 1 H), 6.66 (dd, J = 8.4 Hz, 3 Hz, 1 H), 6.57 (d, J = 3 Hz, 1 H), 4.78 (br s, 1 H), 1.91 (s, 2 H), 1.27 (s, 6 H), 1.28 (s, 6 H); C-13 NMR δ 145.72 (s), 153.09 (s), 143.67 (s), 123.30 (d), 113.98 (d), 109.21 (d), 56.99 (t), 42.36 (s), 41.93 (s), 31.74 (q), 31.42 (q)]. In the case of tosic acid hydrate a third compound, 4-isopropylphenol (rt = 7.9 min.), was also observed as a depolymerization product. The identity of this compound

Table I
Depolymerization of Poly(*t*-BOC-α-methyletyrene) Initiated by Thermal and Photochemical Generators of Acid at 120 °C

acid generator	mode	casting solvent[a]	atmosphere[b]	% depolymerization	mol % comp[c] I	II	III
5 wt % nitrobenzyl tosylate	thermal	C	air (dry)	11	87	13	
5 wt % nitrobenzyl tosylate	thermal	X	air (dry)	16	64	36	
5 wt % tosic acid hydrate	thermal	C	air (dry)	77	45	45	11
5 wt % dinitrobenzyl tosylate	*hν*	C	air (dry)	16	88	12	
5 wt % dinitrobenzyl tosylate	*hν*	C	air (H_2O/saturated)	4	66	34	
5 wt % dinitrobenzyl tosylate	*hν*	C	air (wet/P_2O_5)	10	83	17	
5 wt % triphenylsulfonium hexafluoroarsenate	*hν*	C	air (dry)	14	77	23	
5 wt % triphenylsulfonium hexafluoroarsenate	*hν*	C	air (wet)[d]	8	31	37	32

[a] C denotes cyclohexanone and X denotes xylene. [b] Experiments done on days of high or low atmospheric moisture are denoted as air (wet) or air (dry), respectively. Samples stored during transit on high-humidity days in a P_2O_5 glovebag are denoted air (wet/P_2O_5), and samples stored during transit in a glovebag saturated with water are denoted air (H_2O/saturated). [c] The products are identified as follows: I is 4-hydroxy-α-methylstyrene, II is 5-hydroxy-1,1,3,3-tetramethylindan, and III is 4-isopropylphenol. [d] Substantial amounts of isobutene were detected on pyrolysis of these samples at 725 °C.

was verified by using an authentic sample of material.

By calibration with authentic samples of each of the possible depolymerization products, the GC/MS spectra were used to estimate the percent depolymerization of poly(*t*-BOC-α-methylstyrene) (see Table I). Each entry in this table represents the average of several cohesive runs with an error of ±5%. Note that the depolymerization of polymer samples containing 2-nitrobenzyl tosylate is dependent upon the solvent used to cast the films. When xylene is used, 16% depolymerization is observed; while with cyclohexanone, only 11% depolymerization is seen. Moreover, the ratio of depolymerization products also varies with casting solvent. Specifically, the indan product is more predominant when thermolyzed films were cast from xylene. The reaction with tosic acid hydrate resulted in a high degree of depolymerization, and this may be a consequence of depolymerization occurring during sample preparation.

Photochemically Initiated Depolymerization. Having established the tendency of poly(*t*-BOC-α-methylstyrene) to undergo acid-catalyzed depolymerization, we next investigated whether the same behavior is observed with photochemically generated acid. The resistance of poly(*t*-BOC-styrene) and poly(*t*-BOC-styrene sulfone) to depolymerization was also evaluated. Two photogenerators of acid were studied, triphenylsulfonium hexafluoroarsenate and 2,6-dinitrobenzyl tosylate. Onium salts are well-known, thermally stable photogenerators of acid,[3] while 2,6-dinitrobenzyl tosylate has been shown recently[2] to generate acid efficiently upon irradiation. Unirradiated samples of all the polymers containing either 2,6-dinitrobenzyl tosylate or onium salt showed no detectable sign of polymer depolymerization or *t*-BOC group deprotection when subjected to the postexposure bake temperature (120 °C).

Irradiation of poly(*t*-BOC-α-methylstyrene), poly(*t*-BOC-styrene), and poly(*t*-BOC-styrene sulfone) polymer films containing acid photogenerators resulted in complete removal of the *t*-BOC group during the postexposure bake. In agreement with the thermal experiments using 2-nitrobenzyl tosylate, depolymerization is observed only in the case of poly(*t*-BOC-α-methylstyrene). As can be seen in Table I, depolymerization occurs upon irradiation with both the dinitro and onium salt compounds. Interestingly, it was observed that the percent depolymerization is dependent upon atmospheric humidity. For example, in the case of polymer films containing the dinitro compound, the highest value for depolymerization (16%) was observed in a dry atmosphere, while storage in a glovebag, whose atmosphere was saturated with water, gave the lowest value (4%). During days of high humidity, storage in a low-humidity glovebag results in higher depolymerization (10%); however, even brief exposure to a humid atmosphere during film casting and exposure is sufficient to lower the extent of depolymerization when compared to experiments done under drier conditions. However, under very humid conditions, deprotection of the *t*-BOC group is always complete. Only trace amounts of isobutene are detected during the final pyrolysis of the samples at 725 °C. High atmospheric moisture also tends to give a higher ratio of the indan compound (Table I). Similar observations were made for films containing the onium salt, which tended to give more depolymerization in a dry atmosphere; a humid atmosphere also causes the appearance of a third depolymerization product, 4-isopropylphenol, which had also been observed in the thermolysis of polymer films treated with tosic acid hydrate. In a wet atmosphere, a substantial amount of isobutene was detected during the final pyrolysis of the samples. This may be due either to incomplete deprotection of the *t*-BOC group or, alternatively, to the generation of polyisobutylene during the postexposure bake. Since carbon dioxide was not detected and substantial quantities of oligomers derived from isobutylene were observed, the latter hypothesis appears more likely.

Table II
Effect of Processing Steps on the Molecular Weights of Poly(*t*-BOC-styrene) and Poly(*t*-BOC-α-methylstyrene) Formulated with 5 wt % 2,6-Dinitrobenzyl Tosylate

sample	processing step	$10^{-5}\bar{M}_w$, g/mol	$\bar{M}_w/\bar{M}_n$
poly(*t*-BOC-styrene)	coat	0.27	1.53
	prebake	0.28	1.55
	expose	0.25	1.64
	postexposure bake	0.24	1.67
poly(*t*-BOC-α-methylstyrene	coat	3.45	2.32
	prebake	3.22	3.98
	expose	1.74	2.32
	postexposure bake	1.39	2.96

GPC Evaluation. The tendency of two of the polymers, poly(*t*-BOC-α-methylstyrene) and poly(*t*-BOC-styrene), to depolymerize was evaluated by using GPC analysis that measures the molecular weight of the solid remaining after treatment. The polymers were analyzed after each of the four processing steps during which depolymerization and deprotection may occur, i.e., coating, prebaking, exposure and postexposure baking. The initial results are summarized in Table II for both polymers formulated with 5 wt % 2,6-dinitrobenzyl tosylate. Only a slight decrease (~ 11%) in molecular weight was found for poly(*t*-BOC-styrene) after both exposure and postexposure baking (PEB) whereas a 45% reduction is expected for total de-

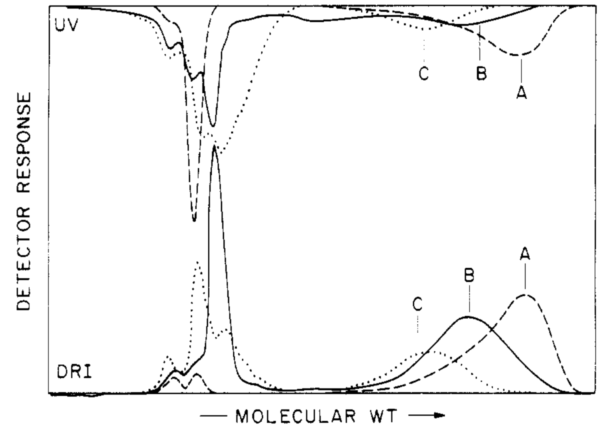


Figure 2. GPC chromatograms of poly(*t*-BOC-α-methylstyrene) formulated with 2,6-dinitrobenzyl tosylate (A, B) and *p*-toluenesulfonic acid (C). The processing conditions were (A) as coated, (B) after postexposure bake, and (C) after postexposure bake. The top, inverted traces were obtained with the UV detector.

Table III
Molecular Weight Changes for Poly(*t*-BOC-α-methylstyrene) Formulated with 2,6-Dinitrobenzyl Tosylate and *p*-Toluenesulfonic Acid Hydrate

additive[a]	process step	$10^{-5}\bar{M}_w$, g/mol	$\bar{M}_w/\bar{M}_n$
none	prebake	3.35	2.79
	expose	3.33	2.92
	postexposure bake	3.16	3.38
2,6-dinitrobenzyl tosylate	prebake	3.29	3.37
	postexposure bake	1.39	2.96
p-toluenesulfonic acid hydrate	coat	0.61	2.27
	bake	0.49	1.91

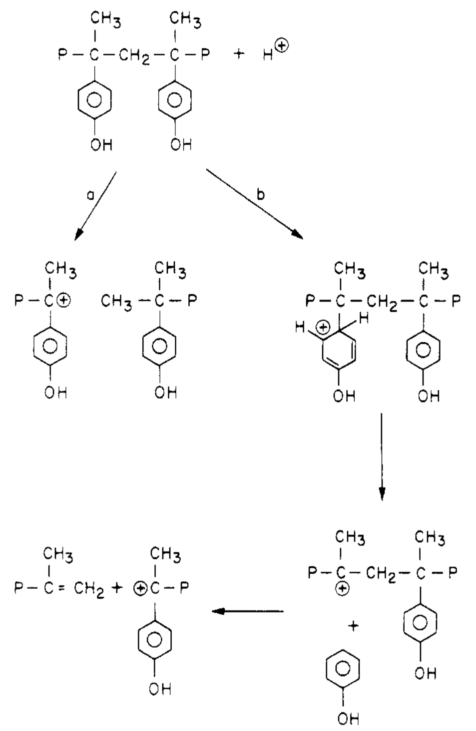
[a] 5 wt % of total solids.

protection (loss of CO_2 and isobutene). Clearly, no depolymerization has occurred, and no significant amounts of low molecular weight products were observed.

In contrast, the analyses for poly(*t*-BOC-α-methylstyrene) (Table II) show striking changes after exposure that are amplified upon PEB to give an ~2.5-fold reduction in molecular weight. This is accomplished by the significant appearance of low molecular weight peaks (Figure 2) in the region where the 2,6-dinitrobenzyl tosylate acid generator elutes. Two of these new peaks differ in retention time from the ester although they do appear to have aromatic groups as judged by their strong response on the 254-nm detector. Extensive depolymerization with formation of monomeric products is consistent with these results. Deprotection cannot be verified by GPC analysis.

To investigate whether *p*-toluenesulfonic acid, the photoproduct from irradiation of the dinitrobenzyl tosylate, gives similar results, mixtures of poly(*t*-BOC-α-methylstyrene) and tosic acid were spin coated onto Si wafers, processed, and analyzed as above for the polymer–ester mixtures. The results are listed in Table III, and a chromatogram for the sample after PEB is presented in Figure 2. Note that a polymer of lower molecular weight was obtained with tosic acid, as compared to the irradiated resist formulated with the dinitrobenzyl ester and processed under the same conditions. Low molecular weight products were formed with tosic acid, but their number and molecular weights are higher than with the photolyzed ester. There is no doubt that tosic acid causes depolymerization of the polymer. Since this depolymerization occurs spontaneously in solution in the presence of free tosic acid, it is not surprising that the extent of depolymerization observed here is greater than that obtained with photochemically generated acid.

Scheme IV

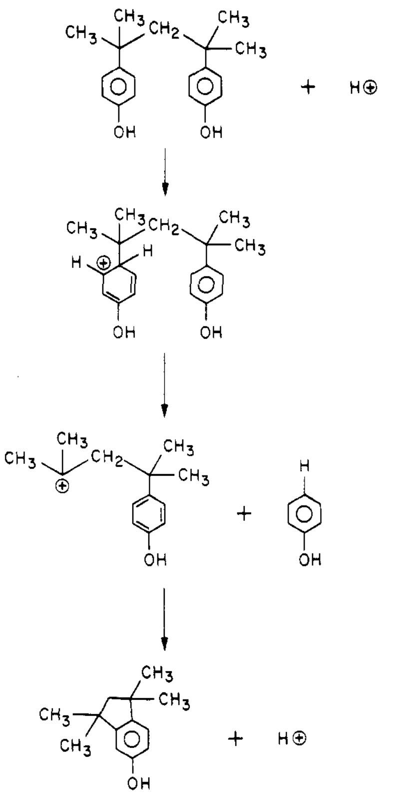


Discussion

Poly(α-methylstyrene) has been reported to undergo depolymerization upon irradiation with ^{60}Co γ-rays.[7-9] It was demonstrated that chain scission and the formation of monomer and dimer (1,1,3-trimethyl-3-phenylindan) occur through a cationic mechanism. Initially, a tertiary carbocation is generated by radiolytic cleavage of the polymer chain. This carbocation can then initiate depolymerization or, alternatively, electrophilically attack a neighboring aromatic ring. In the latter case, a proton is generated that leads to chain cleavage and dimer formation. It follows that addition of a strong acid to poly(α-methylstyrene) should promote chain cleavage. Solution depolymerization of para-substituted poly(α-methylstyrenes), in the presence of strong acid, has in fact been observed.[10] The facility of this reaction in the solid state was confirmed upon thermolysis of poly(α-methylstyrene) in the presence of 2-nitrobenzyl tosylate at 120 °C. The only product detected at this temperature was the dimer 1,1,3-trimethyl-3-phenylindan, which was identified by mass spectroscopy. From these data, it was estimated that ~5% depolymerization occurs. The monomer, although not detected during the low-temperature bake, was observed as the predominant product during the subsequent pyrolysis of the sample at 725 °C. The higher value found for the percent depolymerization of poly(*t*-BOC-α-methylstyrene) under these conditions (Table I) could be explained both by the greater proton affinity of the aromatic ring and by the ability of the electron-donating hydroxyl substituent, freed by loss of the *t*-BOC, to further stabilize a tertiary benzyl carbocation generated upon cleavage of the polymer chain.

In the case of the *t*-BOC-substituted polymer, the monomer, 4-hydroxy-α-methylstyrene, may result from direct proton attack at the carbon–carbon bond or through initial attack onto the aromatic ring to form, in both cases, a tertiary carbocation that would lead to depolymerization (Scheme IV). In route b of Scheme IV, since phenol would be formed only in the initiation stage of the depolymeri-

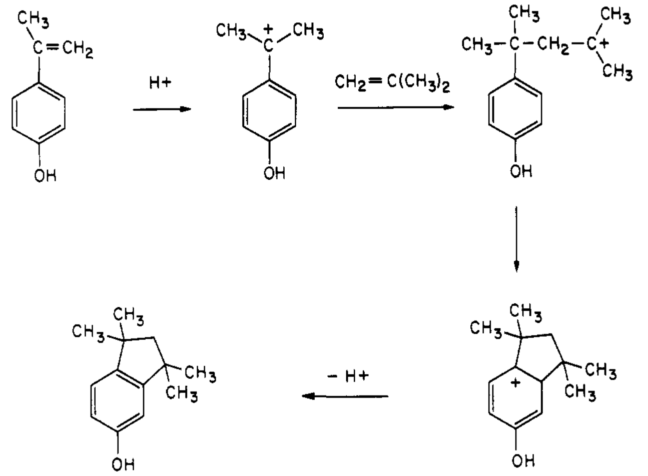
Scheme V



zation reaction, its yield would be much lower than that of the monomer. Thus, failure to observe phenol as a major product would not be surprising. While route a does not generate free phenol, route b is more likely to occur. The second depolymerization product, 5-hydroxyl-1,1,3,3-tetramethylindan, arises from one of two possible pathways. One involves the initial generation of a "dimer", followed by proton-catalyzed decomposition to afford the substituted indan with liberation of phenol (Scheme V). This pathway is unlikely, as phenol was not observed as a major thermolysis product. Moreover, oligomerization of 4-hydroxy-α-methylstyrene with tosic acid at 50 °C, under argon, followed by sublimation (100–200 °C) of the products onto a liquid nitrogen coldfinger did not yield any of the tetramethylindan derivative. Instead, the major products were phenol, and two other compounds identified, on the basis of their mass spectra, as 5-hydroxy-1,1,3-trimethylindan and 5-hydroxy-1,1,3-trimethylindene. These materials probably result from an acid-catalyzed decomposition of the dimer, 5-hydroxy-1,1,3-trimethyl-3-(4-hydroxyphenyl)indan with liberation of phenol. An alternate mechanism involves attack of a 4-hydroxy-α-methylbenzyl tertiary cation onto isobutene followed by an electrophilic cyclization to generate the observed product (Scheme VI) The known reaction of 4-hydroxy-α-methylstyrene with isobutylene to afford the indan product[11] supports this mechanism as the most likely route for the formation of the substituted indan. Additionally, in the presence of an acid catalyst, 4-isopropylphenol and isobutene afford the same product.[12]

The probability of an acid-catalyzed reaction during depolymerization also is indicated by the deleterious effect that water has on depolymerization. Water may act in competition for the protons generated in the polymer film, with the H_3O^+ ion generated having decreased acidity as compared to the "bare" proton. The increase in the relative amount of 5-hydroxy-1,1,3,3-tetramethylindan observed for depolymerizations done with thermally and photochemically generated acid in the presence of moisture

Scheme VI



could thus be explained by a decrease in the rate of depolymerization which would allow more effective attack of the 4-hydroxy-α-methylbenzyl cations onto isobutene before 4-hydroxy-α-methylstyrene can escape from the polymer films. The tendency of the indan compound to be formed in greater proportion in films cast from xylene is not surprising in light of this being a preferred solvent for the synthesis 5-hydroxy-1,1,3,3-tetramethylindan under acidic conditions.[12] The appearance of 4-isopropylphenol as a thermolysis product under certain conditions (Table I) may be due to hydride abstraction by the (4-hydroxy-α-methyl)benzyl cation from the reaction medium. For instance, the *tert*-butyl cation is known to exhibit changes in its ability to abstract hydride upon changes in the acidity of the reaction medium.[13] A similar phenomenon for the (4-hydroxy-α-methyl)benzyl cation may explain our results.

Conclusions

We have demonstrated that depolymerization of poly(*t*-BOC-α-methylstyrene) can be initiated by both thermally and photochemically generated acid. This depolymerization reaction is sensitive to water. The two main products of depolymerization were identified as 4-hydroxy-α-methylstyrene and 5-hydroxy-1,1,3,3-tetramethylindan. We have proposed mechanisms to account for the formation of both compounds. In the future, we plan to investigate this question more closely in addition to evaluating other polymer systems that may be susceptible to this type of depolymerization reaction.

Acknowledgment. We thank E. A. Chandross and A. Shugard for many helpful discussions.

Registry No. Poly(*t*-BOC-α-methylstyrene), 84775-35-9; poly(*t*-BOC-styrene), 87261-04-9; (*t*-BOC-styrene)(SO_2) (copolymer), 120332-58-3; 4-hydroxystyrene, 2628-17-3; 4-hydroxy-α-methylstyrene, 4286-23-1; 5-hydroxy-1,1,3,3-tetramethylindan, 53718-26-6; nitrobenzyl tosylate, 20444-09-1; tosic acid, 104-15-4; 4,6-dinitrobenzyl tosylate, 114719-50-5; triphenylsulfonium hexafluoroarsenate, 57900-42-2.

References and Notes

(1) Ito, H.; Willson, C. G.; Frechet, J. M. J. U.S. Patent 4,491,628, 1985.
(2) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Macromolecules* **1988**, *21*, 2001.
(3) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *317*, 977.
(4) Tarascon, R. G.; Reichmanis, E.; Houlihan, F. M.; Shugard, A.; Thompson, L. F. *Polym. Eng. Sci.*, in press.
(5) Aliev, S. M.; Pokindin, V. K. *Vopr. Neftekhim.* **1977**, 137.
(6) Boon, J. L.; Wetzel, R. J.; Godshalk, G. L. *Limnol. Oceanogr.* **1982**, *327* (5), 839.

(7) Hayashi, K.; Yamamoto, Y.; Miki, M. *Proc. 6th Int. Radiat. Conf.* **1979**, 385.
(8) Hayashi, K.; Yamamoto, Y.; Miki, M. *Macromolecules* **1976**, *9*, 874.
(9) Hayashi, K.; Yamamoto, Y.; Miki, M. *Macromolecules* **1977**, *10*, 1316.
(10) Ito, H.; Willson, C. G.; Frechet, J. M. J. *Macromolecules* **1983**, *16*, 510.
(11) Klein, A. Ger Offen. 2356813, 1975.
(12) Klein, A. Ger Offen. 2304588, 1974.
(13) Olah, G. A.; Schleyer, P. *Carbonium Ions*, Wiley-Interscience: New York, 1970; Vol. II, p 488.

Coil–Stretch Transitions in Mixed Shear and Extensional Flows of Dilute Polymer Solutions

R. G. Larson[*] and J. J. Magda[†]

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974-2070.
Received December 6, 1988

ABSTRACT: A generalization of Zimm's bead–spring model for dilute solutions of flexible polymers that accounts for the influence of coil distortion on hydrodynamic interactions is used to calculate molecular distortions and coil–stretch transitions in general planar flows. Expressing an arbitrary incompressible planar flow as a superposition of a shearing flow and a planar extension, we find that the shearing flow can reduce the critical extension rate $\dot{\epsilon}_c$ required to produce a coil–stretch transition, whereas the original Zimm theory predicts no influence of shearing on $\dot{\epsilon}_c$. The scaling theory of de Gennes predicts a much larger influence of shearing on $\dot{\epsilon}_c$ than is obtained in the bead–spring calculations, apparently because the cylindrical shape assumed by de Gennes does not accurately describe the true pretransition coil shape. The weaker dependence of $\dot{\epsilon}_c$ on shearing found in our calculations is consistent with recent experimental data of Dunlap and Leal.

I. Introduction

Understanding and prediction of the rheological properties of flexible or rigid polymers in dilute solution are of considerable importance, not only because of the technological uses of such polymers as drag-reducing agents or viscosity builders but also because the dilute solution properties can be used to infer molecular structural information such as molecular weight and flexibility. Since the dilute regime of polymer solutions is characterized by the absence of intermolecular interactions, one might suppose that the rheological properties in the dilute regime ought to be easily understood, at least in comparison to concentrated solutions. Although this seems to be true of rigid molecules, understanding of the dilute-solution properties of flexible polymers is still sketchy except in the small deformation regime of linear viscoelasticity. Though it has been known for at least 50 years, for example, that shear thinning occurs when dilute solutions are sheared at high rates, the causes of shear thinning are still not known with confidence.[1]

There are several reasons that the viscoelastic properties of dilute solutions of flexible polymers, despite their seeming simplicity, have been difficult to understand or predict. First, although the chains do not interact with each other, there are *hydrodynamic interactions* between different parts of the same chain.[2] The solvent velocity and hence the drag forces near one part of the chain are influenced by the drag forces acting on other parts of the same chain. The strength of the hydrodynamic interaction between two segments of the chain depends on the separation between the two segments and thus on the chain conformation. Only in the limit of small chain deformation—that is, in the linear viscoelastic limit—is the distribution of chain conformations known a priori. At modest or high deformation rates, the chain conformation distribution and the hydrodynamic interactions are coupled and solution of the coupled problem is difficult unless drastic approximations are made.

A second hurdle impeding understanding of dilute solution rheology is the effect of excluded volume and solvent–polymer interactions on chain conformation in the presence of a strongly distoring flow field. Only in special Θ conditions can this effect truly be neglected.[2]

Despite these and other difficulties, some important qualitative insight has been developed, especially in extensional flows. In particular, it has been recognized for many years that a polymer coil in an extensional flow at strain rates above a critical value undergoes a coil-to-stretch transition in which the molecule unravels to a nearly fully extended state.

More recently it has been appreciated that hydrodynamic interaction can increase the abruptness of this transition. As the polymer molecule is stretched in an extensional flow, hydrodynamic interactions between different parts of the molecule are weakened, thus changing the effective drag force exerted by the solvent on the polymer. Because of hydrodynamic interaction, in the undistorted or nearly undistorted state the drag the solvent exerts on a polymer molecule of high molecular weight is equivalent to the drag that would be exerted on an impenetrable sphere having an effective radius comparable to the radius of gyration of the polymer molecule. This is the so-called "nondraining" picture of the polymer coil. de Gennes[3] and Hinch[4] have extended this picture to the highly distorted state, modeling the deformed polymer as an effective impenetrable cylinder. As the cylinder is extended in an extensional flow, its surface area, and therefore the drag exerted on it by the solvent, increases in proportion to its length. If the distortion of the molecule were to become so severe that hydrodynamic interactions were rendered negligible, then the polymer molecule could be considered a "freely draining" object in which the drag on each portion of the molecule is unaffected by the drag on other portions. The nondraining and freely draining limits are also called the Zimm[5] and Rouse[6] limits, respectively.

de Gennes suggested a simple elastic dumbbell model for the polymer molecule. The dumbbell is characterized

---

[†] Department of Chemical Engineering, University of Utah, Salt Lake City, UT 84112.

0024-9297/89/2222-3004$01.50/0