Table II
Initial Concentration Dependence of $\hat{V}_{FH}$ for Six Systems at 30 °C

system	$[(1/\hat{V}_{FH})(\partial\hat{V}_{FH}/\partial\omega_1)]_{\omega_1=0}$
PSF-TCP	−2.25
PSF-DDS	−2.79
PSF-PNA	−2.99
PPO-DOS	−2.03
PPO-DOP	−2.51
PPO-TCP	−3.26

Calcultions based on eq 22 were carried out for the above six glassy polymer–diluent systems by using estimates for the volumetric, free-volume, and glass transition properties of these systems.[2,3,8,14,15] The results for the mass fraction derivative for $\hat{V}_{FH}$ at $\omega_1 = 0$ are presented in Table II, and it is evident that the theoretical predictions for antiplasticization effectiveness are equivalent to the rankings deduced by Maeda and Paul from their experiments. Consequently, it is fair to conclude that the free-volume equation proposed above appears to provide a reasonable description of antiplasticization effectiveness in glassy polymer–diluent systems.

Acknowledgment. This work was supported by National Science Foundation Grant CBT-8515712 and by funds provided by the Dow Chemical Co.

Registry No. DDS, 80-07-9; PNA, 135-88-6; TCP, 1330-78-5; PPO (homopolymer), 25134-01-4; PPO (SRU), 24938-67-8; DOP, 117-81-7; DOS, 2432-87-3.

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Thermolysis and Photochemical Acidolysis of Selected Polymethacrylates

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ABSTRACT: Thermal behavior and thermolytic deprotection catalyzed by photochemically generated $HSbF_6$ in the solid state have been investigated for atactic polymethacrylates having benzyl, α-methylbenzyl, α,α-dimethylbenzyl, and *tert*-butyl ester groups as well as cyclopropyl carbinol esters. Ease of thermolysis to convert polymethacrylates to poly(methacrylic acid) and to poly(methacrylic anhydride) is very much dependent on the ester groups. The dimethylbenzyl and dimethyl cyclopropyl carbinol esters are converted first to poly(methacrylic acid) and then to anhydride, while poly(*tert*-butyl methacrylate) is rather directly converted to the anhydride due to the higher deprotection temperature, poly(benzyl methacrylate) depolymerizes without much deprotection, and the methylbenzyl ester exhibits depolymerization and deprotection/dehydration. Sensitivity of these polymethacrylates to photochemically induced acidolysis is very much reflected by the thermal deprotection temperatures except for the cyclopropyl carbinol esters, which possess the lowest deprotection temperature in the series but suffer from concomitant rearrangement to a thermally stable primary ester. The thermal rearrangement of the cyclopropyl carbinol ester is more pronounced in the presence of acids. These polymethacrylate films containing a photosensitive acid generator such as arylsulfonium salts can be lithographically imaged in either positive or negative mode depending on choice of a developer solvent owing to the change in polarity resulting from conversion of nonpolar ester to polar acid. Poly(*tert*-butyl methacrylate) allows image reversal owing to its thermal stability at the temperature at which poly(methacrylic acid) and copolymers of methacrylic acid and *tert*-butyl methacrylate undergo anhydride formation.

Introduction

tert-Butyl esters and carbonates readily undergo A_{AL} 1-type acid-catalyzed deesterification in a reaction that does not require a stoichiometric amount of water to produce isobutene/acid and isobutene/carbon dioxide/alcohol, respectively. The polarity change induced by a radiochemically generated acid in the solid state has allowed the design of dual tone resist materials with a very high sensitivity due to the catalytic nature of the reaction (chemical amplification).[2-5] Such polymers included poly(*tert*-butyl methacrylate) (PTBMA), poly(*tert*-butyl *p*-vinylbenzoate) (PTBVB), and poly(*p*-(*tert*-butoxycarbonyloxy)styrene) (PBOCST). Ito et al.[5] have recently studied the effect of the structure of the esters on the photochemical sensitivity of poly(*p*-vinylbenzoates) sensitized with a sulfonium salt cationic photoinitiator and found that the thermal deprotection temperature of these poly(vinylbenzoates) is a good measure of the sensitivity.

PTBMA and poly(methacrylic acid) (PMAA) are converted thermally to poly(methacrylic anhydride) (PMAN) when heated to temperatures above 200 °C as first reported by Grant and Grassie.[6] Matsuzaki et al.[7] have

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found that isotactic PTBMA is smoothly converted to PMAN at 180–200 °C whereas syndiotactic PTBMA exhibits two-step weight loss: deesterification followed by dehydration. Geuskens et al.[8] have found that the rate of water loss is about 4 times faster for isotactic PMAA than for atactic PMAA. The thermal behavior of random copolymers of methacrylic acid and *tert*-butyl methacrylate have been recently studied by Lai.[9] Hatada and coworkers[10] have demonstrated by IR measurement that isotactic poly(α,α-dimethylbenzyl methacrylate) (PDMBZMA) is converted to PMAN at 174 °C as soon as a small amount of deprotection takes place whereas an atactic polymer is predominantly deesterified before its conversion to PMAN. They also showed that these polymers are deesterified to a certain extent upon electron beam exposure.

In this paper we report thermal decomposition behavior of several polymethacrylates and the effect of the ester group on the thermolysis in correlation with the photosensitivity in acid-catalyzed thermolysis.

Experimental Section

Materials. α,α'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. *tert*-Butyl methacrylate was purchased from Aldrich and distilled prior to polymerization. PMAA and poly(benzyl methacrylate) (PBZMA) were obtained from Polysciences. Diphenyl(4-(thiophenoxy)phenyl)sulfonium hexafluoroantimonate was obtained from General Electric and used as a mid UV (300–350 nm) acid generator, which has an absorption centered at 300 nm with ϵ of ca. 20 000.[11]

Synthesis of Methacrylates. α-Methylbenzyl methacrylate was synthesized according to the literature[12,13] in diethyl ether from methacryloyl chloride and *sec*-phenethyl alcohol in the presence of triethylamine. α,α-Dimethylbenzyl, 2-cyclopropylethyl, and 2-methyl-2-cyclopropylethyl methacrylates were prepared by reacting methacryloyl chloride with the corresponding lithium alkoxides in anhydrous tetrahydrofuran (THF).[10] The lithium alkoxides were obtained by treating with *n*-butyllithium (BuLi) α,α-dimethylbenzyl alcohol (Aldrich), cyclopropyl methyl carbinol (Aldrich), and cyclopropyl dimethyl carbinol which was in turn made by reacting cyclopropyl methyl ketone (Aldrich) with methylmagnesium bromide.[14] The synthetic procedure for 2-methyl-2-cyclopropylethyl methacrylate was as follows. Cyclopropyl methyl ketone (16.8 g, 0.2 mol) in 60 mL of anhydrous ether was dropwise added at 0 °C to 100 mL of a methylmagnesium bromide solution (3.0 M in ether). The mixture was stirred at room temperature for 2 days and poured into ice water containing ammonium chloride. The product was extracted with ether and distilled (124 °C/760 mmHg) to give 63% yield. To a solution of 5.0 g (0.05 mol) of dimethyl cyclopropyl carbinol in 60 mL of THF was added under N_2 20 mL of BuLi (2.5 M in hexane). A solution of 4.68 g (0.045 mol) of methacryloyl chloride in 30 mL of THF was added to the resulting mixture after 30 min. The solution was refluxed for 2 h, cooled to 0 °C, and hydrolyzed by adding 100 mL of water. The aqueous phase was extracted with two 50-mL portions of ether and combined with the organic phase. After being dried over magnesium sulfate, the solution was concentrated to give 7.4 g of the crude product. Distillation (30 °C/0.5 mmHg) gave the desired methacrylate in 53% yield. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.75; H, 9.50. 2-Cyclopropylethyl methacrylate was synthesized similarly. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.58; H, 9.31. Synthesis of 2,2-dicyclopropylethyl methacrylate was hampered by rapid hydrolysis of the desired ester.

Polymerization. Radical polymerization of the methacrylates was carried out in toluene or methyl ethyl ketone (MEK) at 60 °C with AIBN as the initiator. A solution of 1.0 g of 2-cyclopropyl-2-methylethyl methacrylate and 5.0 mg of AIBN in 4 mL of MEK was degassed by repeating freeze–thaw cycles under vacuum and heated at 60 °C for 8 h to give 43% of V after precipitation in methanol and drying. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.94; H, 9.71. The polymerization of 2-cyclopropylethyl methacrylate (1.7 g) with AIBN (8.0 mg) in MEK (8.0 mL) was terminated at low conversion (11%) because prolonged reaction resulted in gelation. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.95; H, 9.35.

Scheme I
Polymethacrylates

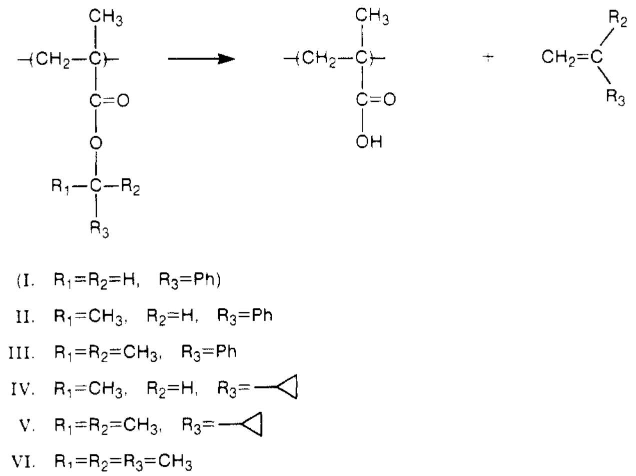


Table I
Physical Properties of Polymethacrylates

no.	R_1	R_2	R_3	M_w[a]	M_n[a]	tacticity,[b] % I	H	S	T_g,[c] °C
I	H	H	C_6H_5	217 700	97 500	4	41	55	40
II	CH_3	H	C_6H_5	1 043 300	114 200	4	35	61	70
III	CH_3	CH_3	C_6H_5	158 500	79 000	9	49	42	80
IV	CH_3	H	C_3H_5	165 300	67 400				82
V	CH_3	CH_3	C_3H_5	135 200	74 400	11	44	45	91
VI	CH_3	CH_3	CH_3	179 500	92 700	6	43	52	120

[a] GPC (relative to polystyrene). [b] ^{13}C NMR. [c] DSC.

Measurements. NMR spectra were recorded in deuteriochloroform ($CDCl_3$) on Varian EM-390 (^1H) and IBM Instruments WP-200 (^{13}C) spectrometers. IR spectra were measured on an IBM IR/32 FT spectrometer. UV spectra were recorded on a Hewlett-Packard Model 8450A UV/VIS spectrometer using thin films cast on quartz plates. Molecular weight determination was made by gel permeation chromatography (GPC) using a Waters Model 150 chromatograph equipped with 6 μStyragel columns at 30 °C in THF. Thus, the molecular weights reported in this paper are polystyrene-equivalent. Thermal analyses were performed on a Du Pont 1090 thermal analyzer at a heating rate of 5 °C/min for TGA and 10 °C/min for DSC under inert atmosphere. GC/MS analysis was carried out by using a Hewlett-Packard 5995A gas chromatograph/mass spectrometer. Film thickness was measured on a Tencor alpha-step 200.

UV Exposure of Polymethacrylate Films. Polymethacrylates were dissolved in cyclohexanone, to which was added diphenyl(4-(thiophenoxy)phenyl)sulfonium hexafluoroantimonate (3.7 mol% to polymer repeating units). Spin-cast films were exposed through a 313-nm bandpass filter to radiation from an Oriel illuminator. Film thickness (1.0 μm) was controlled by adjusting the polymer concentration and spin speed. Imagewise exposure was carried out in a contact mode.

Results and Discussion

The polymethacrylate derivatives investigated in this work are summarized in Scheme I. All the polymers were prepared by radical initiation and are atactic or rather syndiotactic-rich, which could avoid complication due to the effect of tacticity on the thermal behavior of these polymers as discussed earlier. Molecular weights relative to polystyrene, glass transition temperatures (T_g) determined by DSC, and triad tacticities estimated by ^{13}C NMR are summarized in Table I.

TGA (5 °C/min) and DSC (10 °C/min) curves of the polymethacrylates are presented as Figures 1 and 2, re-

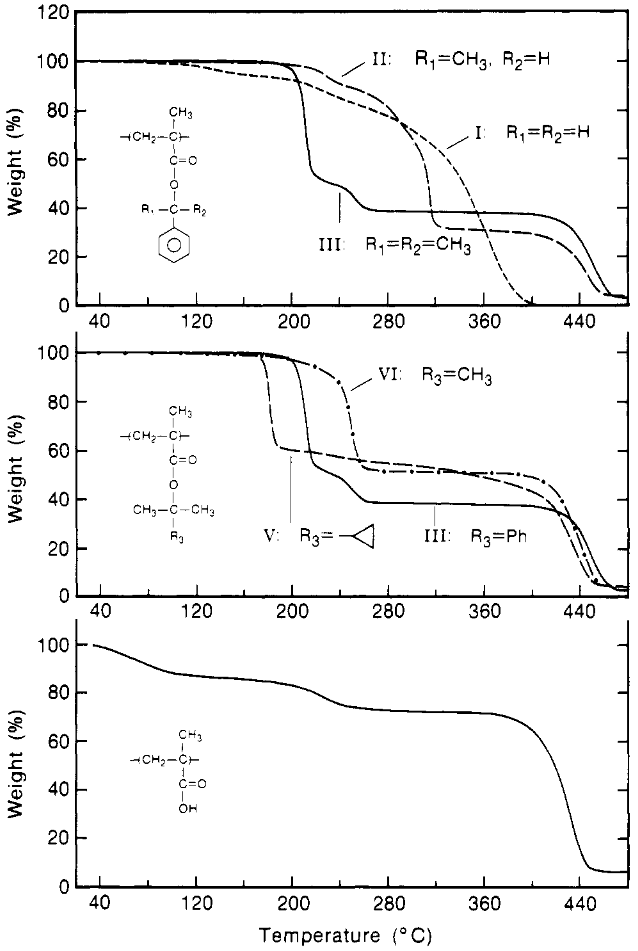
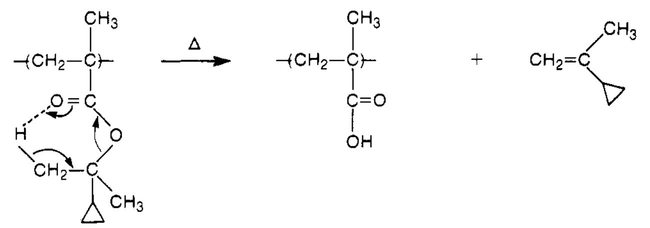


Figure 1. TGA of polymethacrylates and PMAA (heating rate 5 °C/min).

spectively, together with those of PMAA. PMAA loses absorbed water below 140 °C (first heating) and then dehydrates to form PMAN at the temperature ranging from 180 to 260 °C (second heating). The third heating in the DSC shows T_g of PMAN thus produced at ca. 160 °C (159 °C[15]). PBZMA (I) gradually depolymerizes upon heating as is the case with poly(methyl methacrylate) (PMMA) with little deesterification or dehydration, which was confirmed by IR studies of thin films heated at 175–180 °C for 15 min. PDMBZMA (III) exhibits two stages of weight loss between 200 and 260 °C (Figure 1) and two endothermic peaks in DSC (Figure 2), presumably due to the loss of α-methylstyrene at a lower temperature and subsequent dehydration After heating to 360 °C, the second DSC curve shows T_g at 160 °C, indicating complete conversion of III to PMAN. The weight loss observed up to 280 °C in TGA also confirms quantitative loss of α-methylstyrene and water. The volatile product analysis by MS demonstrated in Figure 3 further confirms the observation: III loses α-methylstyrene to form PMAA and dehydration starts at the later stage of the deesterification. Poly(α-methylbenzyl methacrylate) (PMBZMA, II) shows a mixed characteristic of I and III when heated. This polymer deesterifies to release styrene in a temperature range ca. 100 °C higher than that of III and is immediately converted to PMAN as evidenced by T_g observed at 160 °C upon second heating. However, the weight remaining at 360 °C is much smaller than the quantitative loss of styrene and water can account for, suggesting that depolymerization also takes place simultaneously.

PTBMA (VI) quantitatively loses isobutene and water at about 240 °C, as evidenced by the one-stage weight loss that is close to the theoretical value (Figure 1) and the rather broad single endotherm centered at 240 °C (Figure 2). The MS analysis shown in Figure 3 clearly indicates that the deesterification and dehydration are almost simultaneous. Replacement of one of the methyl groups of PTBMA with a cyclopropyl group (V) results in a dramatic decrease in the deprotection temperature by 80 °C (Figure 1). We failed to isolate methacrylic ester of methyl dicyclopropyl carbinol in our attempted monomer synthesis due to the extremely low thermal stability of the ester group. Methyl cyclopropyl carbinol ester of methacrylic acid was successfully synthesized but radical polymerization at 60 °C in solution resulted in gelation especially at high conversions due to the facile hydrogen radical abstraction from the ester methine group. Although DSC in Figure 2 and MS in Figure 3 exhibit well-separated deesterification and subsequent dehydration events in V, TGA (Figure 1) shows only one-step weight loss that is significantly smaller than the quantitative removal of olefin predicts, which is accompanied by gradual loss of weight. T_g of the polymer heated to 360 °C is somewhat lower (ca. 140 °C) than that of PMAN. All these observations indicate that the thermal product from V is not pure PMAN.

Scheme II
Thermolysis of Polymethacrylate of Dimethyl Cyclopropyl Carbinol



V

The carbonyl regions of IR spectra of 1-μm thick films of III and V heated at 180 °C in the air are presented as Figure 4. These polymethacrylates are rapidly converted to PMAA (examination of IR bands at 698 and 762 cm^{-1} of III in a film form revealed that the deesterification had been completed in 15 min) and then to PMAN when baked at 180 °C. The conversion to PMAN is much slower in V than in III, and while III is almost completely converted to PMAN after 68 min at 180 °C, V leaves a significant amount of an absorption due to ester behind even after 98 min as demonstrated in Figure 5. Isothermal TGA at 180 °C of III and V indicates that V loses 37% of its weight (76% of the quantitative loss of olefin and 68% of the quantitative anhydride formation) within 13 min, but extended heating (2 h) results in only a minor weight loss of additional 3% leaving 60% of polymer (74% to the quantitative dehydration) after 2 h while III loses weight at a slower rate to 50% (87% of the quantitative loss of α-methylstyrene and 80% of the quantitative anhydride formation) in 28 min and then slowly keeps losing additional weight upon prolonged heating leaving 45.7% of the original weight (93.9% of the quantitative loss of olefin and 87% of the quantitative dehydration) after 2 h. Prolonged heating beyond 1 h at 180 °C does not degrade V any further, but it seems to take 4 h to completely convert III to PMAN at 180 °C.

The primary pathway of the deesterification is believed to be via a cyclic intermediate to split an olefin (Schemes I and II).[10,16] However, the cyclopropyl carbinol ester (V) may undergo heterolysis of C–O bond to generate the dimethyl cyclopropyl carbenium ion which tends to rearrange itself to the primary cation and recombine with the

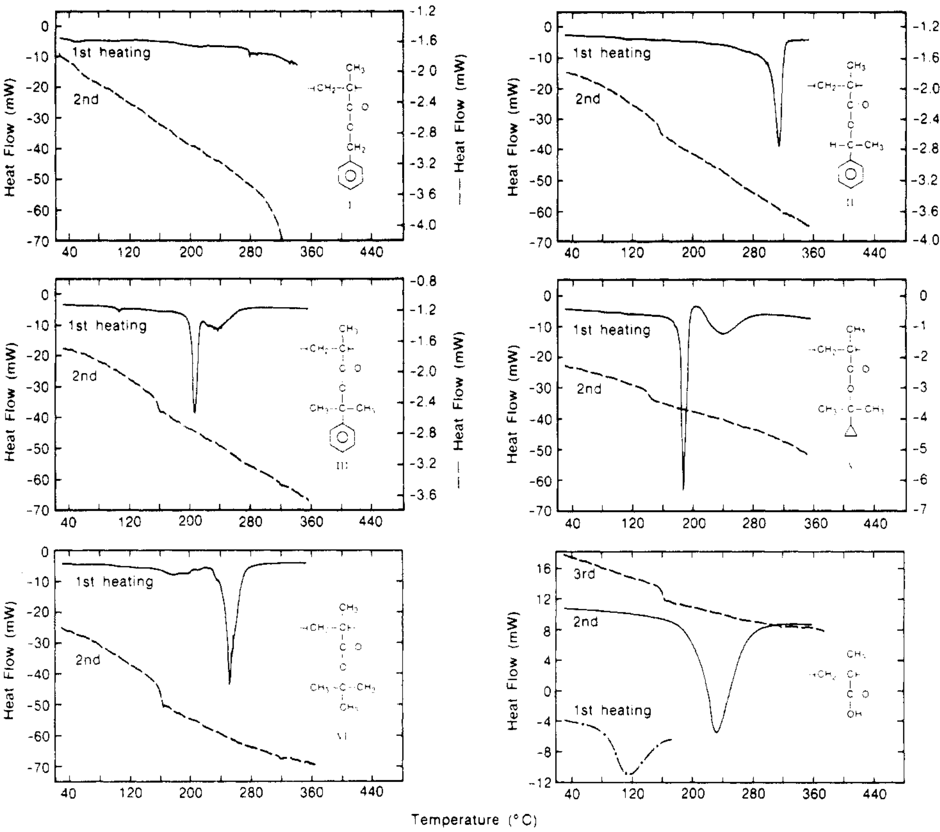
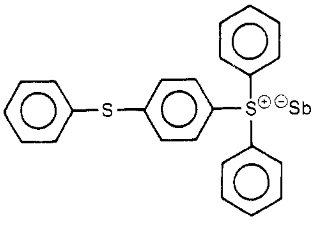


Figure 2. DSC of polymethacrylates and PMAA (heating rate 10 °C/min).

carboxylate to form a rather stable ester VIII (Scheme III). When a film of V was heated at 180 °C, UV absorption below 220 nm drastically increased indicating formation of the C=C double bond. This rearrangement is well-known in the literature.[17]

Aromatic polymers absorb more ultraviolet (UV) light than aliphatic polymers below 300 nm. Therefore, in order to make the optical density constant at a given film thickness while maintaining the sulfonium salt concentration constant, the sulfonium salt VII, (4-(thiophenoxy)phenyl)diphenylsulfonium hexafluoroantimonate,[11] which absorbs in the 300-nm regions where all the polymers in our study are essentially transparent, was used as a photochemical acid generator. As a result, if the sensitizer concentration (mole%) and film thickness are kept constant, optical density of the films at the exposing wavelength (313 nm) can be made constant regardless of the polymer structure. A narrow bandpass filter was used to expose only the sulfonium salt sensitizer.

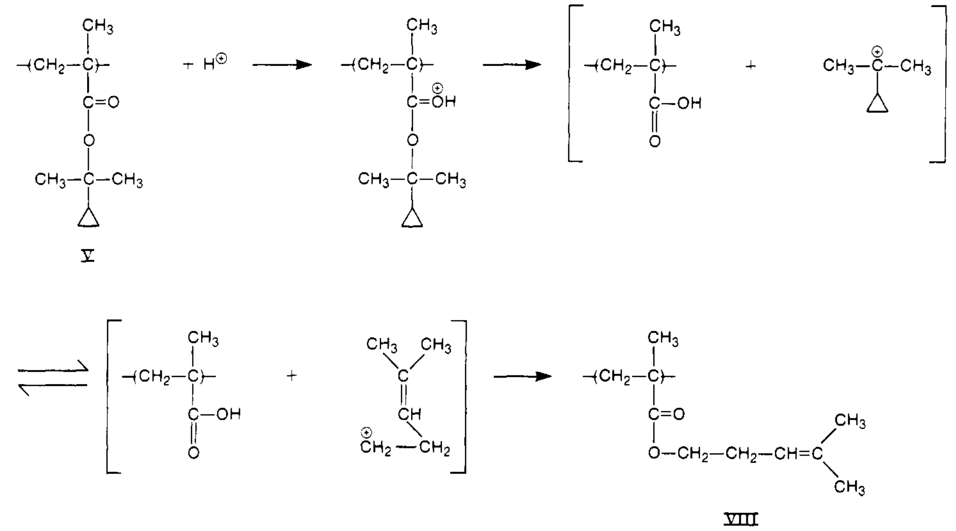


VII

These sulfonium salts generate strong Brønsted acids ($HSbF_6$ in this case) upon irradiation with UV light[11] and have been utilized in the design of very sensitive resist materials.[2-5] The photochemically generated acid catalyzes the thermolysis of the polymethacrylates via A_{AL}-1 type deesterification that does not require a stoichiometric amount of water; that is, the thermal deprotection temperature can be lowered in the presence of acid. In fact, when III in $CDCl_3$ was treated with H_2SO_4 in a NMR tube at room temperature, the polymer NMR peaks disappeared completely due to the precipitation of PMAA and formation of dimers[18,19] or monomer of α-methylstyrene was clearly observed depending on the concentration of the acid. All the polymer films (0.9–1.1 μm) containing VII (3.7 mol % to the polymer repeating units) were prebaked at 100 °C for 15 min to remove the casting solvent, exposed to 313-nm radiation, and postbaked at 135 °C for 2 min. IR spectra before and after exposure are shown in Figure 6. Even I deesterifies to some extents at a high acid concentration (high-exposure dose) while thermolysis in the absence of acid does not induce appreciable deprotection. Introduction of methyl groups into the benzylic carbon dramatically increases the sensitivity, and III undergoes almost 75% conversion to PMAA even at 2.1 mJ/cm^2, as expected from the reduced deprotection temperature of pure polymers. The deprotection reaction can be quantitatively followed by examining the disappearance of IR bands at 696–698 and 750–762 cm^{-1} in the case of the benzyl methacrylates.

However, the dimethyl cyclopropyl carbinol ester V does not reflect the lowest deesterification temperature in the acid-catalyzed thermolysis (Figure 6). The IR carbonyl bands of V exposed to a very high UV dose (200 mJ/cm^2) and postbaked at 180 °C for 3 min are essentially the same as those of an unexposed but postbaked film (Figure 7). In contrast, the peaks at ca. 3000 cm^{-1} before and after UV exposure are completely different indicating occurrence of the rearrangement reaction discussed earlier. Both unexposed and exposed films of V were heated at 180 °C for a longer period of time (93 min) to investigate the effect of the photogenerated acid on the extent of the rearrangement. IR spectra of the unexposed and exposed films baked at 180 °C for 93 min are provided in Figure 8. The IR spectra of the exposed film clearly show that there are

Scheme III
Acid-Catalyzed Thermolysis of Polymethacrylate of Dimethyl Cyclopropyl Carbinol



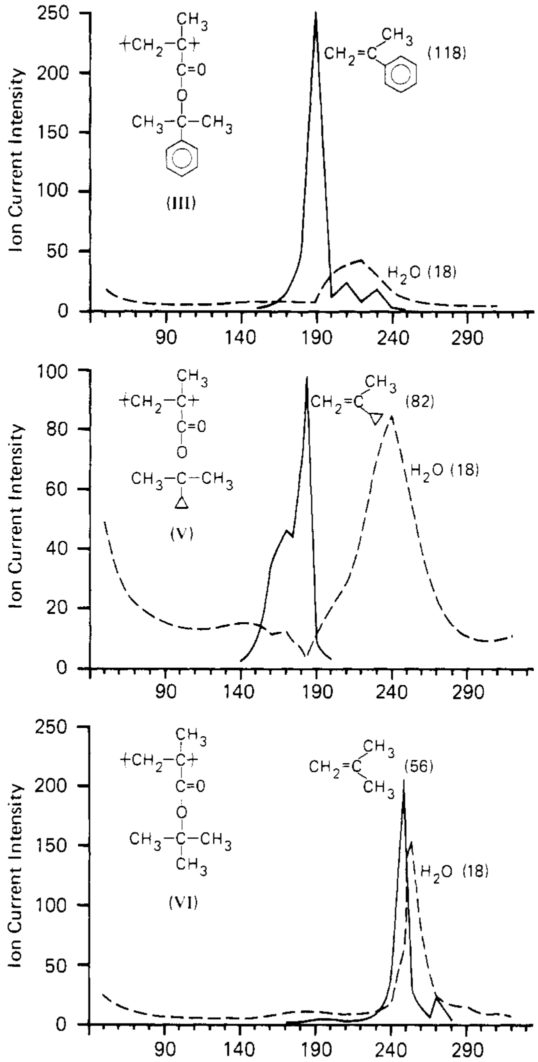


Figure 3. MS analysis of olefins and water released from heated polymethacrylates.

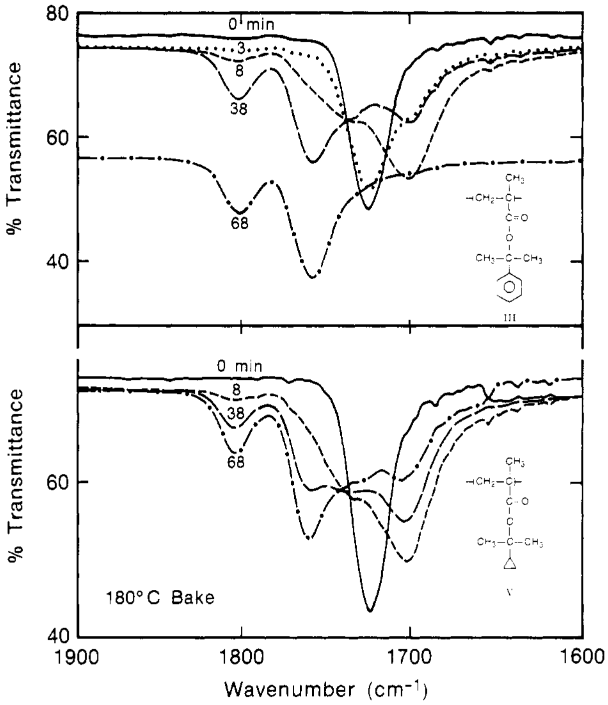


Figure 4. IR carbonyl bands of III and V heated at 180 °C.

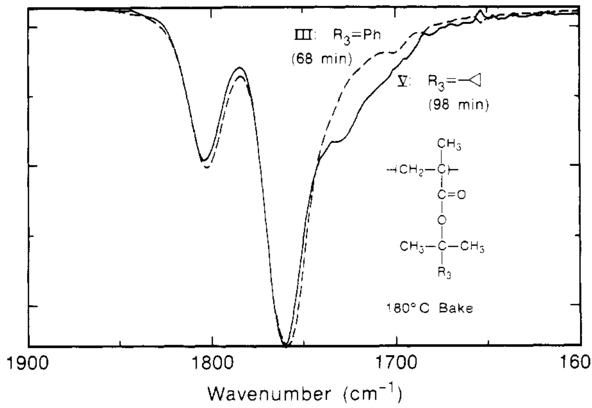


Figure 5. IR carbonyl bands of III and V heated at 180 °C showing incomplete dehydration in V.

a large amount of acid and ester remaining even after 93 min at 180 °C whereas the unexposed film has been more completely converted to PMAN with only a small amount of acid and ester remaining as discussed earlier. Figure 8 clearly indicates that the rearrangement is much more predominant in the thermolysis of V in the presence of acid than in the absence of the catalyst. The thermolysis proceeds to PMAA via the six-membered intermediate

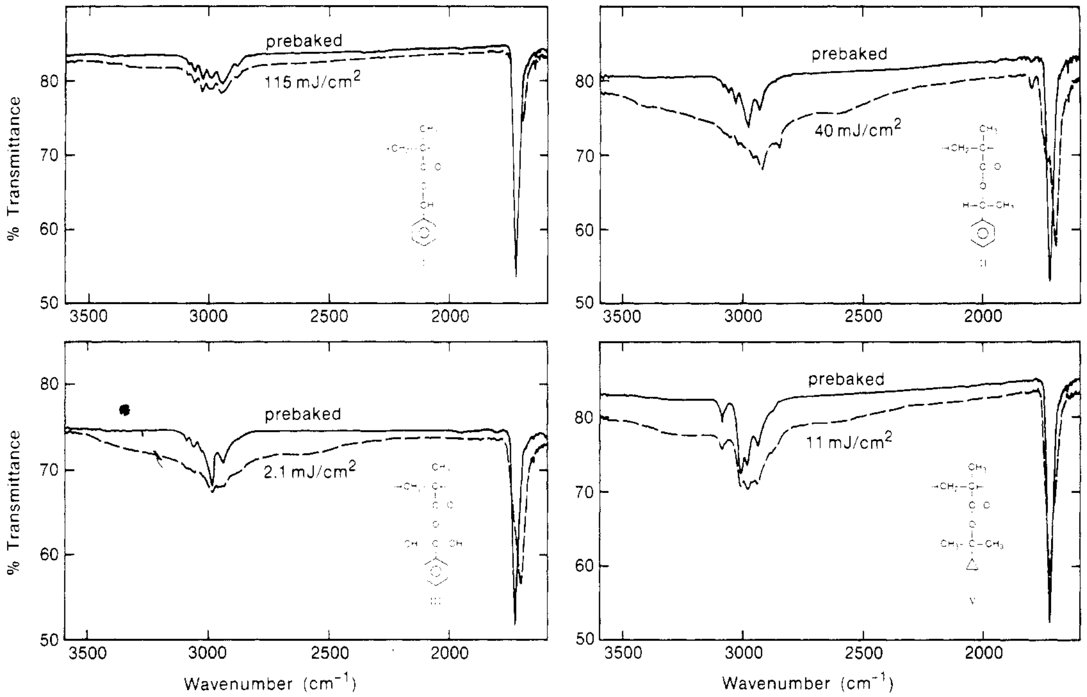


Figure 6. IR spectra of polymethacrylate resist films containing 3.7 mol % of VII before and after UV irradiation.

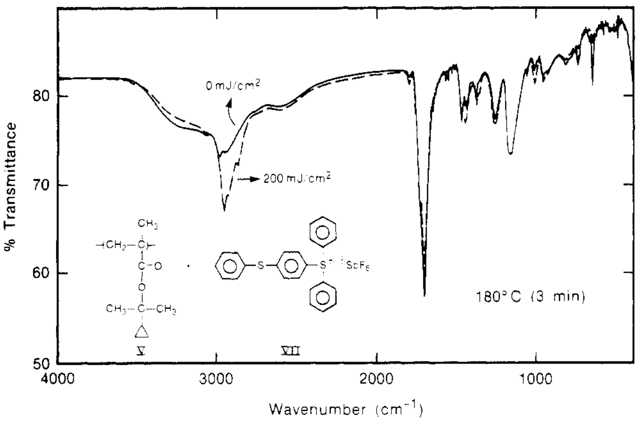


Figure 7. IR spectra of unexposed and exposed films of V containing 3.7 mol % of VII heated at 180 °C for 3 min.

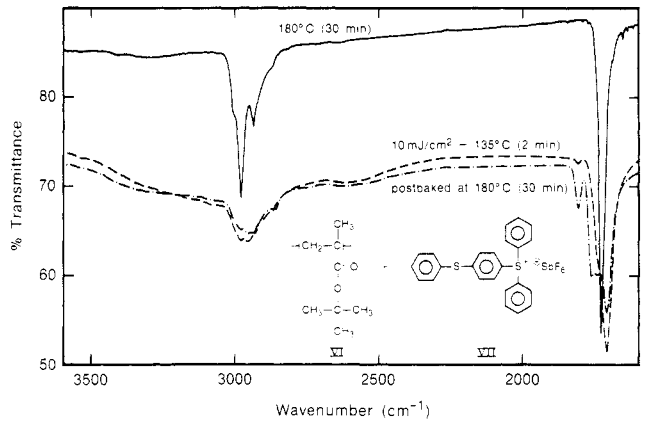


Figure 9. IR spectra of PTBMA VI resist containing 3.7 mol % of VII baked at 180 °C prior to UV exposure, exposed to 10 mJ/cm² followed by brief bake at 135 °C, and postbaked at 180 °C.

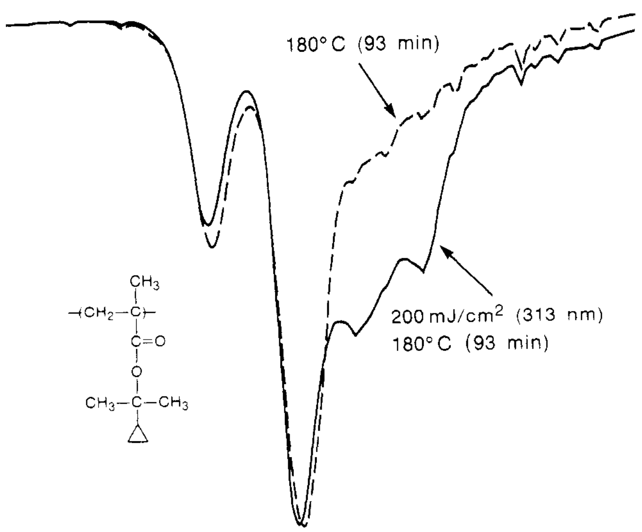


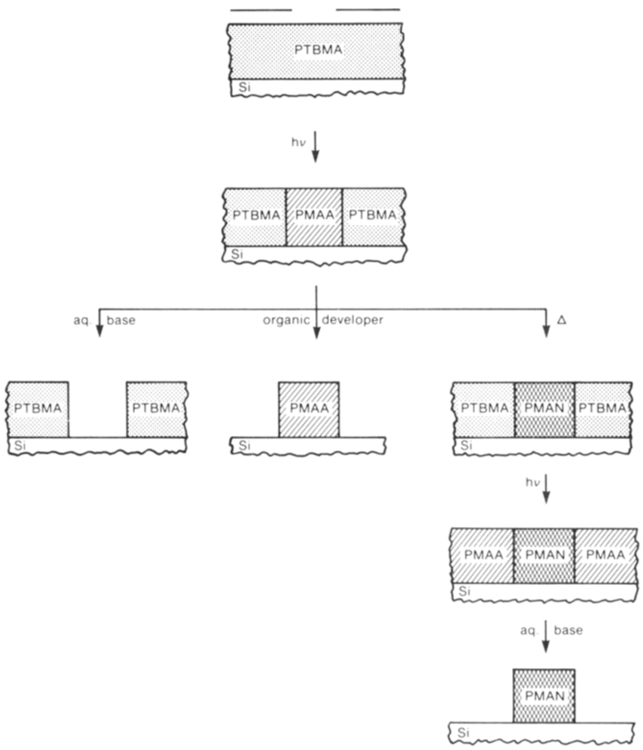
Figure 8. IR carbonyl bands of V heated at 180 °C in the presence and absence of photochemically generated $HSbF_6$.

involving H of the ester methyl groups with a minor concomitant rearrangement (Scheme II). The acid-catalyzed thermolysis induces heterolysis of the C–O bond to produce the dimethyl cyclopropyl carbenium ion that could eliminate H^+ to form an olefin but is prone to rearrangement to form a primary cation that could recombine with the methacrylic acid (Scheme III). Thus, the thermally stable ester VIII once formed intercepts the dehydration involving the neighboring groups, leaving a significant amount of the methacrylic acid groups unreacted.

The photochemical sensitivity of VI lies between II and III as the thermal analysis predicts (Figure 9). The *tert*-butyl ester is thermally quite stable and does not show much deprotection at 180 °C as evident from TGA, DSC, MS, and IR (Figure 9) studies. PMAA and copolymers of methacrylic acid and *tert*-butyl methacrylate undergo a facile anhydride formation at this temperature as demonstrated by Lai[9] and by Figure 9. In consequence, it should be possible not only to image the sensitized PTBMA in either a positive (aqueous base development) or negative (organic developer) mode but also to reverse the image (negative imaging in aqueous base) by following the sequences shown in Scheme IV.

A film of PTBMA containing a sulfonium salt is imagewise exposed to UV radiation followed by a brief heating at 90–140 °C, which converts the exposed regions

Scheme IV
Processes of Producing Lithographic Images in PTBMA Utilizing Radiation-Induced Polarity Change

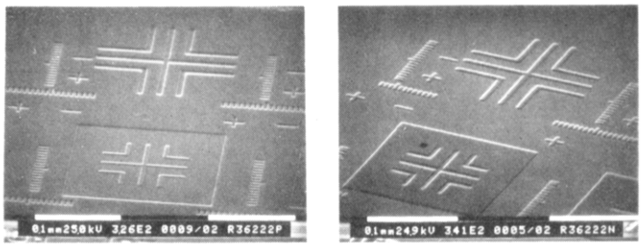


to PMAA (or copolymer of *tert*-butyl methacrylate and methacrylic acid depending on the dose). If one chooses aqueous base as a developer, the exposed regions are selectively dissolved away, leaving a positive image of the mask. Use of an organic developer such as chlorobenzene allows a negative-tone imaging because this developer dissolves only PTBMA in the unexposed areas. Heating of the imagewise exposed wafers at elevated tempeatures (180 °C) converts PMAA in the exposed areas to PMAN (or terpolymer of *tert*-butyl methacrylate, methacrylic acid, and methacrylic anhydride depending on UV exposure dose and/or heat treatment conditions) which is insoluble or less soluble in aqueous base. Subsequent flood UV exposure followed by a brief baking at ca. 100 °C converts PTBMA in the originally unexposed regions to PMAA. In consequence, development in aqueous base results in formation of negative relief images (image reversal). III will not provide the image reversal due to the low thermal stability of the ester polymer. II could reverse the image at a much higher dose. While poly(vinylbenzoates) can be imaged in either positive or negative mode owing to the large change in polarity that has been induced by the photochemically generated acid, it should be very difficult to reverse the image because the dehydration (presumably intermolecular) takes place at very high temperatures (320–340 °C).[5] Scanning electron micrographs of the relief images printed in the PTBMA resist are provided as Figure 10.

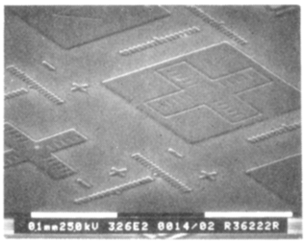
Summary

1. Thermal behavior and photochemically induced acid-catalyzed deesterification were investigated in the solid state for atactic polymethacrylates bearing benzyl, α-methylbenzyl, α,α-dimethylbenzyl, *tert*-butyl, and cyclopropylmethyl ester groups.

2. Ease of thermolysis to convert polymethacrylates to PMMA and to PMAN is very much dependent on the ester structure.



(a) Positive: AZ2401/H_2O = 1/5 (b) Negative: Chlorobenzene



(c) Image Reversal (Negative): AZ2401/H_2O = 1/5

Figure 10. Scanning electron micrographs of images printed in PTBMA resist in three modes depicted in Scheme IV.

3. While PBZMA depolymerizes without undergoing deesterification, the dimethylbenzyl ester is converted upon heating to PMAA first and then to PMAN. The methylbenzyl ester undergoes anhydride formation at about 300 °C with simultaneous depolymerization.

4. Atactic PTBMA is thermally deesterified at about 240 °C with almost simultaneous dehydration.

5. Replacement of one of the methyl groups of PTBMA with a cyclopropyl group results in a dramatic decrease in the deprotection temperature by 80 °C. The thermal deesterification and dehydration events are clearly separated in the dimethyl cyclopropyl carbinol ester. A minor rearrangement to a more thermally stable primary ester takes place concomitantly during the thermal deesterification of the cyclopropylmethyl ester.

6. Acid catalysis reduces the deprotection temperatures, thus totally seprating deesterification from dehydration.

7. Susceptibility of these polymethyacrylates to deesterification catalyzed by photochemically generated $HSbF_6$ is very much reflected by the deprotection temperature of pure polymers except for the cyclopropylmethyl esters. The rearrangement of the cyclopropylmethyl ester is more pronounced in the presence of the acid than in the pure polymer.

8. These polymethacrylates containing a photochemical acid generator can be lithographically imaged in a positive (aqueous base developer) or negative mode (organic developer) due to the large polarity change caused by acid-catalyzed thermolytic deesterification. PTBMA allows image reversal (negative patterning with aqueous base) because PMAA formed in the exposed regions can be converted to PMAN by heating at elevated temperatures at which PTBMA in the unexposed is stable.

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Registry No. I, 25085-83-0; II, 25085-84-1; III, 56963-83-8; IV, 113686-67-2; V, 113686-69-4; VI, 25189-00-8.

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Theory of Crystallizable Block Copolymer Blends

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ABSTRACT: We present an equilibrium theory of blends incorporating diblock copolymers in which one of the copolymer blocks is crystallizable and the other is amorphous. The material is assumed to order in a lamellar structure of alternating semicrystalline and amorphous layers with the chemical bonds which connect the copolymer blocks lying in the interfacial regions between the layers. The amorphous blocks are modelled as flexible chains, each with one end (the joint) anchored in an interface. Their contribution to the free energy is calculated via the self-consistent solution of the modified diffusion equations. The crystalline regions are modelled as folded chains, also with one end in an interfacial region (bonded to the corresponding end of an amorphous block). In this paper, we specialize to the case of pure copolymer. We find that the calculated amorphous block free energies can be expressed as a single universal function depending on the total degree of polymerization of the amorphous block, its stretching, and a parameter proportional to the thickness of the interface. We have fitted an analytical form to this function, which can be used for any amorphous block, and we have combined it with our model of the crystallizable block to obtain an analytic expression for the lamellar thickness. As an example, the theory is applied specifically to PEO-*block*-PS copolymers.

1. Introduction

Block copolymers, one of whose components is crystallizable (for example, polyethylene oxide) while the other component is noncrystallizable (such as atactic polystyrene), have been studied extensively[1-11] and shown to possess equilibrium lamellar structures which can be obtained by annealing, usually in the presence of a preferential solvent for the amorphous domains. Unlike crystallizable homopolymers, where the chain folding is metastable, folding of the partly crystallizable blocks of copolymers exists at equilibrium, in which case it is governed by a balance of the thermodynamic forces between the crystalline and amorphous domains.[12] It is the purpose of this paper to give a detailed account of the origin of the various contributions to the overall free energy of such a system, thereby arriving at a theory of the equilibrium state. We carry out this program by further developing the statistical mechanics of inhomogeneous multicomponent polymeric systems, along the same lines as Hong and Noolandi,[13] and solving the appropriate mean field equations for the polymer chain distribution functions.

At first sight, the case of partly crystallizable block copolymers (we will assume diblock copolymers and lamellar morphology for the generic calculation given later) appears to be easier to treat than noncrystalline block copolymers, as we are clearly in the strong segregation limit, with no interpenetration of blocks and well-defined domain boundaries. However, the connectedness of the blocks of the copolymers imposes severe restrictions on the molecular conformations and gives rise to an intimate connection between the structural properties of the amorphous and crystalline domains. For example, at a given molecular weight and composition, compression of the amorphous domains can be accommodated to some extent by increasing the number of folds in the crystalline domains, thereby decreasing the average separation of the chain stems exiting from the crystalline region. The overall change in the free energy associated with this kind of molecular rearrangement is one of the main predictions of our theory. The equilibrium domain sizes are determined by packing constraints as well as the balance of the total energy of chain folding in the crystalline domains with the associated entropic conformational and stretching free energy of the noncrystallizable blocks in the amorphous domains.

The theoretical work presented in this paper is also of general interest for the understanding of the boundary conditions imposed on the solution of the modified diffu-

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