prepared following literature procedures.

Addition of Difluorocarbene to I. Under an atmosphere of purified nitrogen, 0.1 g of I,[10] CF_3HgPh (see Table I), and a 3-fold molar excess with respect to CF_3HgPh of NaI were placed in a 50-mL round-bottom flask equipped with a reflux condenser and a Teflon-covered magnetic bar. To this mixture was added 25 mL of degassed benzene. The solution was vigorously stirred and heated at reflux for 25–30 h. The mixture was cooled to room temperature and filtered. The solvent was removed by evaporation under reduced pressure. The polymer, dissolved in 3 mL of THF, was precipitated from a large excess of methanol. This purification process was repeated. The polymer was dried under vacuum for 24 h. Yields between 89 and 95% of difluorocyclopropanated polymers were obtained.

Addition of difluorocarbene to II was carried out as above. The product polymer was obtained in 90% yield after the methanol precipitation.

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Vinylidene Chloride–Methyl Methacrylate Random Copolymers: Sequence Length Effects on IR Spectra and Thermal Stability

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ABSTRACT: Two series of vinylidene chloride–methyl methacrylate (VDC/MMA) random copolymers, prepared by batch free radical polymerization in solution, were examined by DSC for thermal transitions, T_g and T_{ll}, as reported elsewhere. The thermal analysis was accompanied by thermal decomposition with lactone formation and foaming, both known from prior literature. Quantification of the decomposition reaction is reported here. In one series, the initial monomer ratio was kept equimolar and the percent conversion varied; in the other, the initial VDC/MMA monomer ratio was varied. FTIR studies have shown that, in the solid state, the observed C=O frequency of the MMA units is a function of sequence length and distribution in the copolymers. The TGA studies show that the thermal stability of the copolymers is also a function of sequence length and distribution. The thermal degradation is maximized when the number of adjacent MMA and VDC units is at a maximum and the primary mode of thermal decomposition involves intramolecular cyclization via loss of both methyl chloride and HCl to form an unsaturated lactone. The structure of the resultant lactone has been characterized by FTIR analysis.

Introduction

We have previously reported[1] the synthesis, characterization, and differential scanning calorimetry (DSC) studies of two series of vinylidene chloride–methyl methacrylate (VDC/MMA) random copolymers. In one series, the initial VDC/MMA monomer ratio was varied; in the other, the initial monomer ratio was kept equimolar, and the percent conversion for the polymerization was varied. It was shown that both the glass transition (T_g) and the liquid–liquid transition (T_{ll}), as detected by DSC, varied linearly as a function of copolymer composition in both series.

In an attempt to gain additional insight into the types of interaction (both inter- and intrachain) occurring in this copolymer series, we have examined the variation of the carbonyl stretching frequency in both copolymer series. Also, because of foaming and/or decomposition problems, which complicated the earlier DSC analyses,[1] we have examined the thermal stability of these samples by thermogravimetric analysis (TGA).[2]

Experimental Section

Synthesis and Characterization. Synthesis and characterization data for both VDC/MMA copolymer series have been previously reported.[1]

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Fourier Transform Infrared Spectroscopy. Spectra were recorded of thin films cast directly onto KBr plates from either THF or $CHCl_3$. The film thickness was such that the intensity of the carbonyl band was in the range 0.2–0.8 absorbance units, thus assuring adherence to Beer's Law. The films were dried in a vacuum oven at elevated temperature (60 °C for films from $CHCl_3$ or 90 °C for films from THF) until no bands due to the solvent could be detected; this typically required 48–96 h. Spectra were recorded at room temperature with a Nicolet 20-DXB spectrometer (Nicolet Analytical Instruments, Madison, WI); 100 scans at a resolution of 1.0 cm^{-1} were normally collected.

Thermogravimetric Analysis. TGA analyses were done on a Du Pont 951 TGA module interfaced with a Du Pont 1090 Thermal Analyzer (Du Pont Instruments, Wilmington, DE). Samples were normally 10–15 mg (loose or compacted powder) contained in open Al pans; samples were heated from 30 to 250 °C at a rate of 5 K/min under a constant purge (100 mL/min) of dry nitrogen.

Sequence Length Estimations. We have previously shown[1] that classical copolymerization kinetics (terminal model) quite adequately described the copolymer compositions in this series, and this result is also consistent with prior literature data.[3] We were thus able to estimate sequence lengths of both VDC and MMA units in each copolymer.[4]

Results and Discussion

The studies reported here were inspired by the classical studies of Wessling et al. on the variation of T_g with composition for copolymers of VDC with a variety of comonomers.[5] Using carefully selected comonomers, he attempted to isolate the effects of a number of parameters (steric and polar interactions, the effect of symmetry, and copolymer microstructure) on the T_g vs composition behavior of VDC copolymers. He was also the first to suggest that polar interactions (between chains and/or between adjacent units of the same chain) of VDC units and carbonyl groups of comonomer units are significant.

Also relevant to the current work are the extensive studies on blends of halogen-containing polymers with carbonyl-containing polymers.[6-10]

FTIR Studies. On the basis of the blend studies cited above (and many others), it can be predicted that the C=O frequency due to MMA units should shift to *lower* frequency as the VDC content of the MMA/VDC copolymers increase if *interchain* VDC–MMA interactions were of most importance in determining the position of the carbonyl band. Similar frequency shifts have been reported for the C=O band of methyl isobutyrate, as a model for PMMA, with various halogenated solvents.[10] There does not, however, seem to be any clear understanding of the detailed nature of the interaction. Miscibility in such blend systems is most often attributed to the formation of a hydrogen bridge, C···H···O=C, between the carbonyl oxygen and an acidic C–H bond, although dipole–dipole interactions between chains have also been suggested.[11,12] Such interactions have also been treated as Lewis acid–base interactions by Fowkes;[13] he considers the carbonyl oxygen of the ester to be a Lewis base (electron donor) which can form acid–base interactions with electron-accepting (acidic) sites on other molecules. Wessling has shown that PVDC can act as a Lewis acid.[14]

If *intrachain* VDC–MMA interactions (between adjacent units on the same chain) were the major factor determining the position of the carbonyl band, then one would expect the maximum shift in the C=O frequency to occur near the midrange of composition. Such interactions have been proposed to explain the T_g vs composition behavior for a number of VDC copolymers.[5] More recently, Dent and Boyer[15] have found that both the *Tg* vs composition curve and the T_{ll} vs composition curve for vinylidene chloride–methyl acrylate exhibit a clear maximum at about equimolar composition. They also have shown that the frequency shift of the poly(methyl acrylate) carbonyl band (by FTIR) shows the same type of dependency.

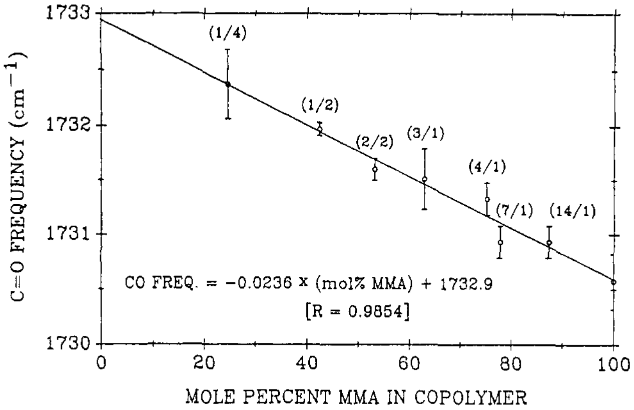


Figure 1. Variation in the C=O frequency as a function of mole percent MMA for the MMA/VDC composition series. The numbers in parentheses are the average sequence lengths (MMA/VDC) rounded to the nearest whole number. The error bars have a total length of 2 standard deviations.

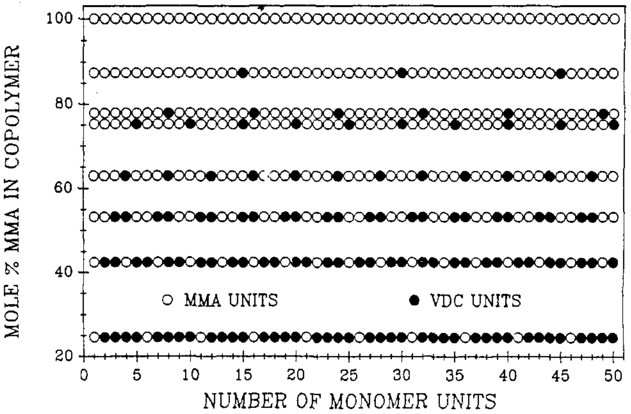


Figure 2. Approximate sequence distributions for the MMA/VDC composition series. Each circle represents one monomer unit; average sequence lengths (as shown in Table I) have been rounded to the nearest whole unit.

The variation of the C=O frequency as a function of mole percent MMA in the copolymer for the composition series is shown in Figure 1. The frequency of the carbonyl band varies in essentially a linear manner from 1730.6 to 1732.4 cm^{-1} as the VDC content of the copolymer increases from 0 to 75.4 mol %. This result is clearly inconsistent with both predictions cited above but is, we believe, understandable when one considers sequence–length distributions in these copolymers.

Table I summarizes the *calculated* sequence lengths for both the composition series (MK3.12 through MK3.92) and the conversion series (BS-1 through BS-11). Though we have not experimentally determined sequence lengths or sequence length distributions, this system seems to be well described by classical copolymer kinetics, as evidenced by experimentally determined copolymer compositions agreeing very well with those calculated by the copolymer composition equation. We therefore assume that the resultant copolymers are statistical, and we have no experimental evidence to suggest any "blockiness". Figure 2 schematically represents the microstructure of a 50-unit portion of the polymer chain for each sample in the composition series. At high MMA content, individual MMA units are adjacent to other MMA units, and there is dipole–dipole interaction between the carbonyl *carbon* of one MMA unit and the carbonyl *oxygen* of an adjacent MMA

Table I
Characterization Data[a] for MMA/VDC Copolymers

code	wt % MMA[b]	M_w[c]	M_n[c]	M_w/M_n	average seq length MMA[d]	average seq length VDC[d]
MK3.12	100.0	228000	128000	1.78		
MK3.22	87.4	140000	84000	1.67	14.49	1.05
MK3.32	77.8	97000	56000	1.73	6.61	1.11
MK3.42	75.2	93000	54000	1.72	4.19	1.19
MK3.52	62.9	54000	27000	2.00	2.83	1.33
MK3.62	53.2	51000	32000	1.59	2.12	1.54
MK3.72	42.4	46000	29000	1.59	1.58	2.05
MK3.82	24.6	37000	25000	1.48	1.22	3.77
MK3.92	0.0	ND[e]	ND	ND		
B5-1	ND	ND	ND	ND	3.31	1.26
B5-2	ND	ND	ND	ND	3.16	1.28
B5-3	ND	ND	ND	ND	3.14	1.28
B5-4	ND	ND	ND	ND	2.78	1.34
B5-5	ND	ND	ND	ND	2.73	1.35
B5-6	ND	ND	ND	ND	2.46	1.42
B5-7	ND	ND	ND	ND	2.06	1.57
B5-8	ND	ND	ND	ND	1.79	1.77
B5-9	ND	ND	ND	ND	1.52	2.17
B5-10	ND	ND	ND	ND	1.07	9.78
B5-11	ND	ND	ND	ND	1.00	>100

[a] For further details, see ref 1. [b] Determined by IR or NMR. [c] By GPC relative to polystyrene standards. [d] Calculated from copolymerization kinetics. [e] ND = not determined.

unit; this interaction can occur through a conformationally favorable six-membered ring. This interaction decreases the C=O bond order, resulting in the C=O frequency occurring at a *lower* frequency than that in an "unassociated" MMA unit. Conversely, in the copolymer containing 75% VDC, Figure 2 shows that, on the average, single MMA units are isolated from one another by four intervening VDC units; there is little or no MMA–MMA interaction. The C=O frequency in this case thus approximates that of an "unassociated" MMA unit. Thus, the VDC units are functioning as "spacers", and the frequency variation seen does not depend on the chemical nature of the VDC units. This also suggests that there is little or no attractive interaction between VDC and MMA units; this is in line with the intermolecular interaction reported by Challa.[10] We believe that similar results would be observed for MMA copolymers containing noninteractive functional groups. Conversely, one would expect that an MMA copolymer containing a comonomer unit capable of forming strong dipole–dipole interactions with carbonyl groups would exhibit the inverse behavior. As these strongly interacting units were incorporated, the ester–ester dipole interaction would be replaced by stronger dipole–dipole interactions between the ester carbonyl and the comonomer dipole. As part of work currently in progress, we have examined the variation of the C=O frequency in a series of MMA–acrylonitrile (AN) random copolymers.[16] In that series, the C=O frequency varied from 1731.3 cm^{-1} (high MMA content) to 1728.2 cm^{-1} (high AN content), consistent with our hypothesis.

There have been many studies of association phenomena in stereoregular PMMAs, both in solution and the solid state, since the phenomenon was first reported by Fox in 1958.[17] Notable examples include the early work of Rehage using X-ray, NMR, and viscosity techniques;[18] light-scattering and proton NMR studies by Spevacek and co-workers;[19] IR and Raman studies of films and solutions by Dybal and co-workers;[20] recent work by Spevacek et al. using IR and NMR spectroscopy, wide-angle X-ray scattering (WAXS), and electron microscopy;[21,22] and recent studies by Challa and co-workers using differential scanning calorimetry (DSC), WAXS, solution viscometry, and isothermal mixing calorimetry.[23,24] These studies have focused primarily on intermolecular association in the well-known stereocomplex of PMMA formed by mixing solutions of isotactic and syndiotactic PMMA.[25] In support of our hypothesis that intramolecular association is present in atactic PMMA, work by both Rehage[18] and Spevacek[19] suggests that such intramolecular association in atactic PMMA can be detected in solution. Also, NMR studies by Spevacek and Schneider[26] show that intramolecular association is present in dilute solutions of syndiotactic PMMA. We have observed no evidence of splitting of the C=O band in our samples into more than one symmetrical peak; such splitting has been ascribed to intermolecular aggregates in stereoregular PMMAs.[21,22]

Similar (though smaller) shifts in the C=O frequency were also observed for the conversion series. The C=O frequency was essentially at the position predicted on the basis of the copolymer composition and reached its maximum value when the VDC/MMA sequence length ratio was at the maximum.

TGA Studies. During our DSC studies of both series of copolymers,[1] it was observed that some of the DSC samples underwent extensive foaming and/or carbonization. The thermal degradation of PVDC and VDC-containing copolymers is well documented[27-30] and normally involves thermally initiated loss of HCl forming poly(chloroacetylene) units and long polyene sequences leading to color formation.

We have studied the thermal degradation in both series of VDC–MMA copolymers by TGA. Results for the composition series are shown in Figure 3, where three different temperatures characteristic of the decomposition (the onset temperature and the temperatures at which 1% and 2% weight loss have occurred) are plotted versus mole percent MMA in the copolymer. The three smooth curves (simply fitted by a quadratic equation) pass through a distinct minimum at approximately 50 mol % MMA which, based upon the estimated sequence lengths shown in Table I, is the region in which the number of adjacent MMA–VDC units would be a maximum. This relationship is shown schematically in Figure 4, in which the ratio (longer sequence length/shorter sequence length) is also plotted versus mol % MMA in the copolymer. These results allow us to conclude that the ease of thermal degradation in this series is a function of the number of adjacent MMA–VDC units and that the primary mode of thermal decomposition

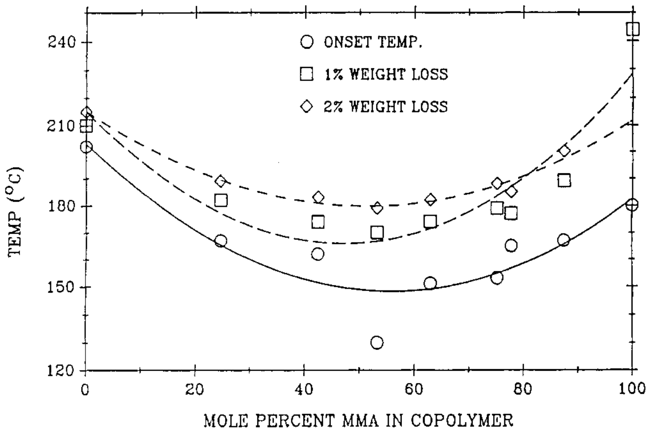


Figure 3. Various decomposition temperatures (as shown in the legend) for the MMA/VDC composition series. The smooth curves through the data sets are quadratic fits.

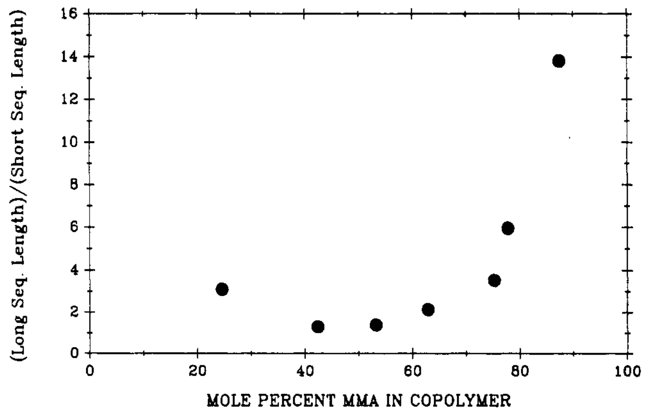
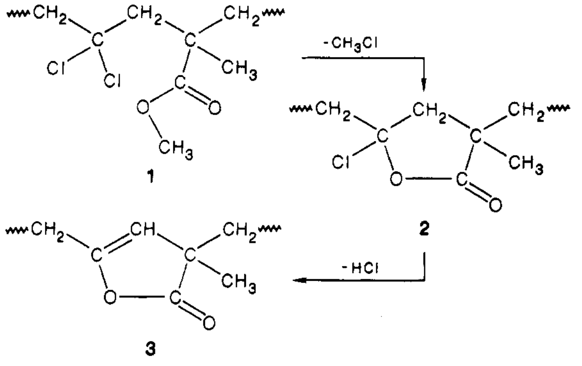


Figure 4. Ratio (longer/shorter) of sequence lengths for the MMA/VDC composition series.

below 250 °C involves an intramolecular reaction between adjacent MMA and VDC units, leading to lactone formation as shown below (1 → 2):



Our IR data (see below) confirm lactone formation and suggest that at least some further dehydrochlorination has occurred leading to unsaturated lactone formation (2 → 3). We show this dehydrochlorination process occurring after lactonization, but we cannot totally eliminate that HCl loss occurs before cyclization.

This thermal lactonization has ample precedent in the work of both Johnston and Harwood[31,32] and Zutty and Welch.[33,34] Also, the 1968 work of Burnett, Haldon, and Hay on MMA-VDC copolymers[35] reported unsaturated lactone formation and suggested that lactonization preceded loss of HCl.

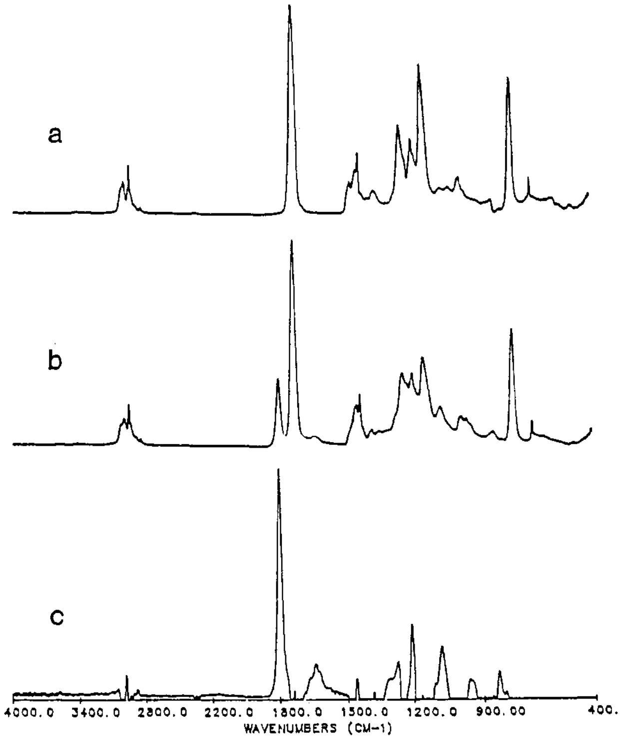
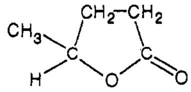


Figure 5. FTIR spectra of a MMA/VDC copolymer containing 42.4 wt % MMA: (a) before thermal degradation; (b) degraded for 1 h at 190 °C in a nitrogen atmosphere; (c) difference spectrum (b–a). The three spectra have different scales for the y (absorbance) axis, with the absorbance scale chosen to have the most intense peak at full scale.

In order to further elucidate the structure of the cyclized material, we have carefully compared the IR spectra of a sample before and after thermal decomposition. A MMA/VDC sample containing 42.4 mol % MMA was subjected to isothermal degradation at 190 °C in the TGA apparatus for varying lengths of time. The extent of lactonization (as evidenced by determining the intensity of the lactone carbonyl relative to that of the methacrylate carbonyl) increased approximately linearly as a function of degradation time at various temperatures greater than 120 °C. Figure 5 (a and b) compares the total IR spectra (4000–400 cm^{-1}) of a sample before and after degradation for 1 h at 190 °C. Also included in Figure 5c is the difference spectrum obtained by balancing out the strong PMMA carbonyl peak at ca. 1730 cm^{-1}. The most intense peak in the difference spectrum is the C=O peak at 1798.7 cm^{-1}. Figure 6a shows the difference spectrum in the 1850–1550-cm^{-1} region, Figure 6b shows the difference spectrum in the 1700–1550-cm^{-1} region, and Figure 6c shows the 1000–750-cm^{-1} region. We believe that these spectral data confirm that both lactonization and dehydrochlorination have occurred. If only cyclization had occurred, one would expect the lactone carbonyl to occur quite near that of the saturated five-membered-ring lactone (γ-valerolactone, 4), which exhibits C=O absorption at 1770 cm^{-1}.[36] There is, however, excellent correspondence between the carbonyl peak we observed in cyclized material and that which has been reported for α-angelica lactone (5) at 1799 cm^{-1}.[36] We also note (Figure 6a) the presence of significant absorption in the range 1680–1620 cm^{-1}, the region in which C=C stretching vibrations normally occur. Figure 6c shows that the strongest band occurring in the difference spectrum in the range 1000–650 cm^{-1} is at 832.5 cm^{-1}; the C–H out-of-plane bending frequency for trisubstituted cycloolefins is reported to occur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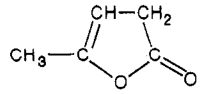
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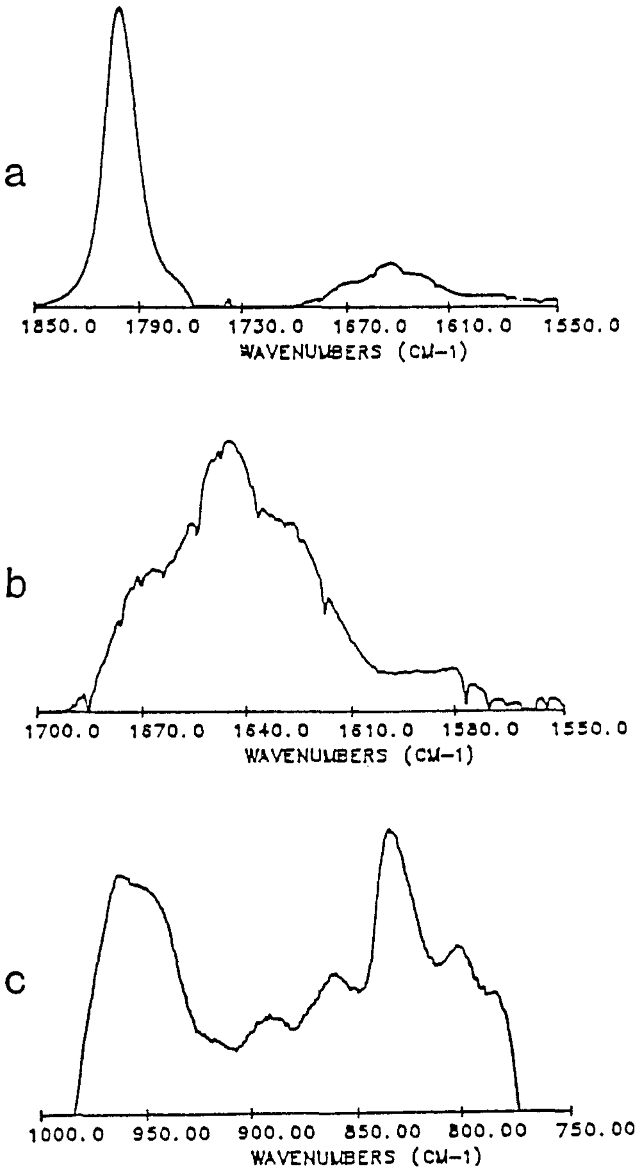

Figure 6. Selected regions, with expanded x and y (frequency and absorbance) axes, for the difference spectrum shown in Figure 5c. The absorbance axes are chosen such that the most intense peak is full scale: (a) 1850–1550 cm^{-1}; (b) 1700–1550 cm^{-1}; (c) 1000–750 cm^{-1}.

in the range 840–790 cm^{-1},[37] and this band occurs in α-angelica lactone at 836.5 cm^{-1}.[36]

Summary and Conclusions

Two series of vinylidene chloride–methyl methacrylate random copolymers have been examined by both FTIR spectroscopy and thermogravimetric analysis (TGA). Results of these studies allow the following conclusions to be drawn.

1. The vinylidene chloride units function as inert "spacers" and decrease the intramolecular association between carbonyl dipoles of MMA units.

2. The C=O stretching frequency increases in a linear fashion as a function of vinylidene chloride content in the copolymer, up to approximately four VDC units per MMA unit, as indicated in Figure 1.

3. The VDC–MMA copolymers exhibit varying thermal stability with maximum susceptibility to thermal decomposition occurring when the number of adjacent MMA and VDC units is at a maximum.

4. Thermal decomposition proceeds via intramolecular cyclization and loss of HCl from adjacent VDC and MMA units to form an unsaturated five-membered-ring lactone.

5. The structure of the resultant unsaturated lactone unit has been characterized by FTIR difference spectroscopy as being a β,γ-unsaturated γ-valerolactone moiety.

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Registry No. (MMA)(VDC) (copolymer), 25120-29-0.

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

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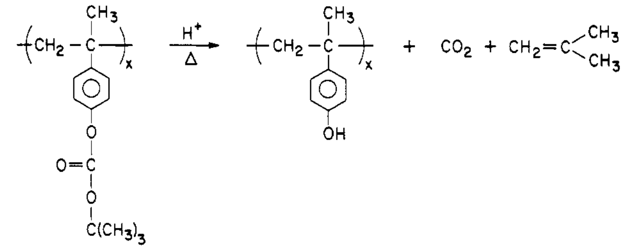
ABSTRACT: The thermolysis and acidolysis of three polymers, poly(4-((*tert*-butoxycarbonyl)oxy)-*α*-methylstyrene) [poly(*t*-BOC-*α*-methylstyrene)], poly(4-((*tert*-butoxycarbonyl)oxy)styrene) [poly(*t*-BOC-styrene], and poly(4-((*tert*-butoxycarbonyl)oxy)styrene sulfone) [poly(*t*-BOC-styrene sulfone)], 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.

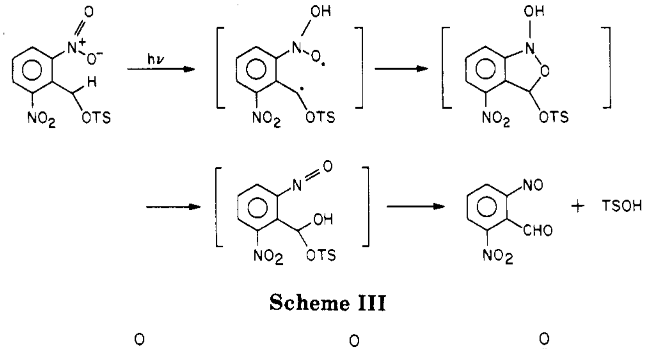
Introduction

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.

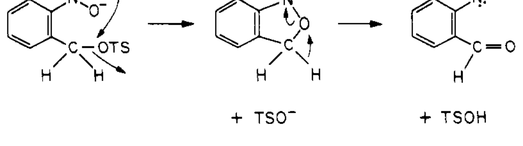
Scheme I



Scheme II



Scheme III



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.

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

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