Polymer Bulletin 26, 297–303 (1991)

Polymer Bulletin

Cationic curing of polymer coatings: Evaluation of *o*-nitrobenzyl tosylate as a thermally labile acid precursor

James F. Cameron and Jean M. J. Fréchet*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301, USA

Summary

The propensity of *o*-nitrobenzyl tosylate to act as a thermal source of *p*-toluenesulfonic acid useful in the cationic curing of polymers was established both in solution and the solid state using a combination of variable temperature ^{1}H NMR and quantitative infrared spectroscopy. Monitoring of the thermal generation of *p*-toluenesulfonic acid within inert coatings of poly(styrene) or poly(methyl methacrylate) confirmed that the process was most efficient at temperatures between 100 and 110°C, though slow liberation of acid was observed at temperatures as low as 90°C.

Introduction

The *o*-nitrobenzyl group is a well known protecting group which is typically cleaved photochemically [1]. The photo efficient removal of the *o*-nitrobenzyl moiety has led to its widespread use in a diverse array of applications. For instance, besides use as a protecting group in standard organic transformations, the efficiency of the solid state *o*-nitrobenzyl photorearrangement has resulted in its use in the microelectronics industry: *o*-Nitrobenzyl carboxylates have been used as dissolution inhibitors in resist formulations [2] while *o*-nitrobenzyl sulfonates have found use as sources of photogenerated acid [3,4]. Furthermore, *o*-nitrobenzyl derived carbamates have been developed as sources of photogenerated amines, diamines and polyamines [5-6].

More recently, the thermal stability of the *o*-nitrobenzyl group as present in *o*-nitrobenzyl tosylate has attracted some attention [3]. Originally, interest in this material arose from its potential as a photochemical source of p-toluenesulfonic acid but, in this regard, it proved somewhat unstable towards the standard processing conditions required of such photoacid precursors [3]. This observation led to a realization that the thermal decomposition of *o*-nitrobenzyl tosylate may allow for the thermal generation of acid. Currently there are several well documented sources of thermally generated acid among which, ammonium sulfonates and benzoin tosylate are the most commonly known [7]. In addition, a large number of diaryliodonium [10] and various sulfonium salts [11, 12] with suitable counterions such as AsF_6^-, PF_6^-, etc., have been shown to possess interesting properties as thermal precursors of acid [12]. Interest in these materials is mainly due to their potential application as curing agents in coating and paint technology. More recently, thermally generated p-toluenesulfonic acid has found use in the image reversal of a negative resist via the novel method of inhibiting the curing action of the acid by photogenerating base in the exposed areas [8].

Based on our current interest in the area of novel curing processes for coatings as well as imaging systems, we report here the results of our investigation into the thermally sensitive nature of *o*-nitrobenzyl tosylate with emphasis being placed on the ability to control the thermal generation of *p*-toluenesulfonic acid in solution and in the solid state. Direct applications of this thermally sensitive acid precursor in the areas of novel polymer coatings and in the chemistry of resists will be described in forthcoming publications.

---

*To whom offprint requests should be sent

Results and Discussion

The first indication of the thermally sensitive nature of *o*-nitrobenzyl tosylate was gained through Differential Scanning Calorimetry (DSC). The DSC curve of *o*-nitrobenzyl tosylate shows two transitions (Fig. 1); the first at 101°C, is endothermic and corresponds to the melting point while the second transition appears almost immediately after melting. This latter peak is strongly exothermic and corresponds to the decomposition of the material.

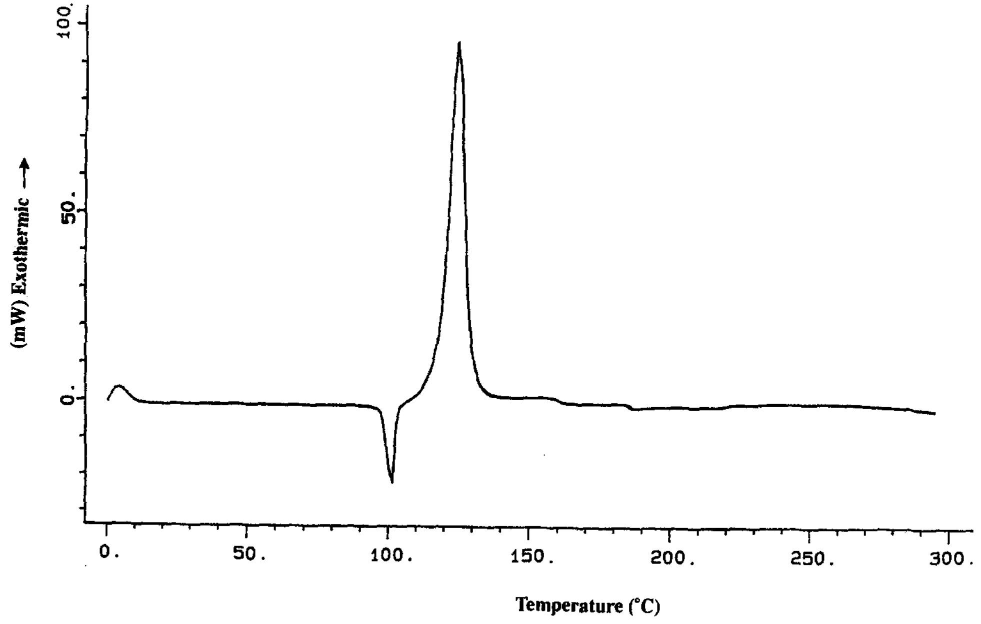
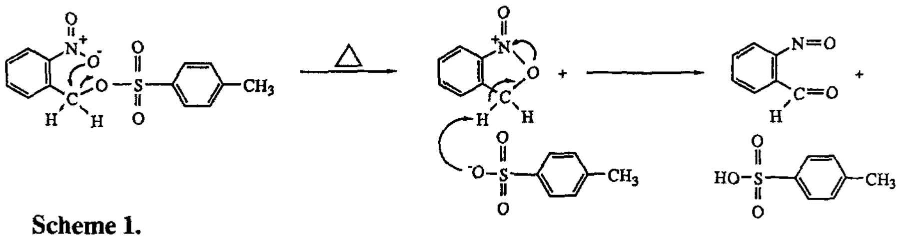


Figure 1. Differential scanning calorimetry trace for *o*-nitrobenzyl-tosylate.

The decomposition temperature was confirmed by dynamic thermogravimetric analysis (TGA) which showed the start of a substantial weight loss occurred on heating *o*-nitrobenzyl tosylate above its melting point. The extent of thermolysis was found to be independent of the purge gas used as experiments under both nitrogen and air gave similar degrees of decomposition. Interestingly, isothermal TGA showed that the material was decomposing slowly even at 90°C with a 0.2% weight loss occurring over 30 min. After such heating, the appearance of the *o*-nitrobenzyl tosylate suggested that it had undergone substantial decomposition as evidenced by its black color, but ^{1}H NMR analysis showed its purity to exceed 99%. On the other hand, ^{1}H NMR spectroscopy of the residue from a similar isothermal TGA run performed at 110°C indicated that complete decomposition of *o*-nitrobenzyl tosylate to *p*-toluenesulfonic acid had occurred over 30 min.



Scheme 1.

In mechanistic terms, the thermal generation of *p*-toluenesulfonic acid likely proceeds by an internal displacement of tosylate by the *o*-nitro group (Scheme 1). This explanation has previously been offered for the decomposition of other *o*-nitrobenzyl tosylates [9] and is essentially a thermal version of the well known photo-redox pathway of cleavage. This mode

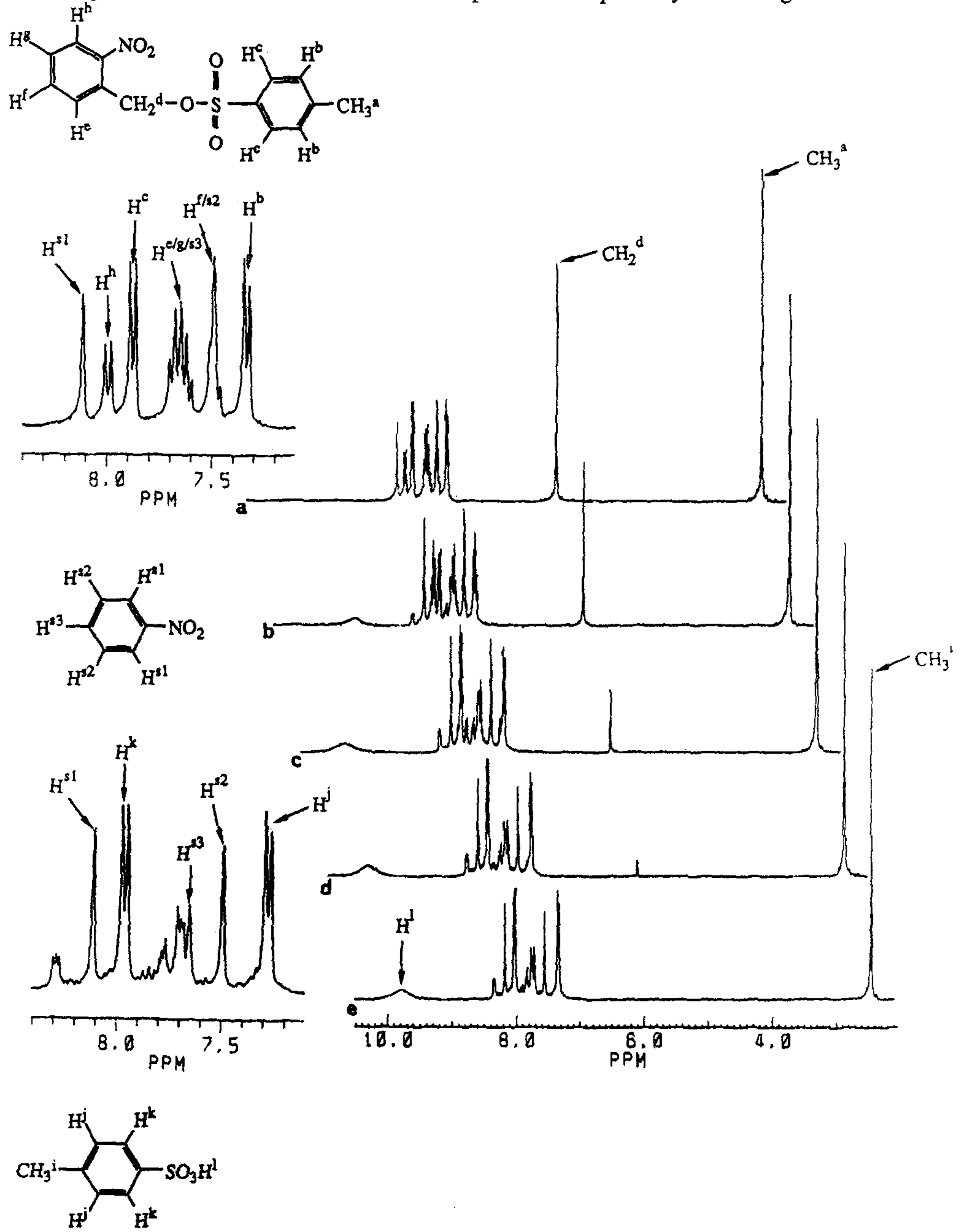


Figure 2: Change in the ^1H NMR spectrum of *o*-nitrobenzyl tosylate on heating at 105°C in nitrobenzene-d_5; a) Prior to heating; b) 48 min; c) 100 min; d) 153 min; e) 205 min.;

of cleavage necessitates the formation of *o*-nitrosobenzaldehyde as a thermal byproduct. Our experiments confirm that this is the case and ^{1}H NMR spectroscopy on the decomposition products of *o*-nitrobenzyl tosylate in dimethylsulfoxide-d_6 show an aldehydic resonance at δ10.27 along with the expected resonances of *p*-toluenesulfonic acid.

The thermal decomposition of *o*-nitrobenzyl tosylate in solution could also be followed conveniently by variable temperature ^{1}H NMR spectroscopy in nitrobenzene-d_5. The result of one such study, performed at 105°C, is shown in Fig. 2 and illustrates the facile thermal generation of *p*-toluenesulfonic acid. On heating, the benzylic resonance (CH_2^d) at δ 5.61 slowly disappears as does the AB quartet of the sulfonate at δ 7.33 (H^b) and 7.90 (H^c). Similarly, the resonance of the proton ortho to the nitro group (H^h) at δ 8.02 disappears while the change in the other *o*-nitrobenzyl resonances (H^{e-g}) remains partially hidden by the solvent resonances at δ 7.50 (H^{s2}) and 7.67 (H^{s3}). In addition, the characteristic AB quartet at δ 7.28 (H^j) and 7.96 (H^k) of *p*-toluenesulfonic acid appears along with the exchangeable sulfonic acid resonance (H^l) at δ 9.72.

By monitoring the disappearance of the benzylic methylene resonance (CH_2^d) at δ 5.61 in relation to the methyl resonance ($CH_3^{a,i}$) at δ 2.36, the percent *p*-toluenesulfonic acid generated with increasing heating time could be readily calculated from the ^{1}H NMR integration. The integral ratio $[I(CH_2^d)/ I(CH_3^{a,i})]$ was calculated before and after heating. The ratio of the amount of *o*-nitrobenzyl tosylate present after heating to the amount present initially multiplied by one hundred gives the percent *o*-nitrobenzyl tosylate remaining after heating (Eq. 1). From this the percent *p*-toluenesulfonic acid generated was found by subtraction (Eq. 2). A plot of these % conversion values against heating time is shown in Figure 3.

$$\text{\% Tosylate Remaining After Heating} = \frac{\text{Final } [I(CH_2^d)/ I(CH_3^{a,i})]}{\text{Initial } [I(CH_2^d)/ I(CH_3^{a,i})]} \times \frac{100}{1} \qquad \text{Eq. 1}$$

$$\text{\% } p\text{-Toluenesulfonic Acid Generated} = 100 - \text{\% Tosylate Remaining} \qquad \text{Eq. 2}$$

The solid state thermolysis of *o*-nitrobenzyl tosylate was monitored by coating sodium chloride disks with 1μm thick polymer films [typically polystyrene or poly(methyl methacrylate)(PMMA)] containing up to 10 mol % of *o*-nitrobenzyl tosylate and following the changes in the infrared spectrum of these films on heating. In this way , the conversion of the nitro group to a nitroso moiety could be readily followed by observing the disappearance of the asymmetric and symmetric N-O stretching bands at 1530 and 1400-1325 cm^{-1} respectively. The observed change in the infrared spectrum on heating a polystyrene film containing 10 mol % *o*-nitrobenzyl tosylate on a hot plate at 110°C is shown in Fig. 4 and is consistent with the proposed mode of thermolytic cleavage in which the nitro group is reduced to a nitroso group.

Using a quantitative infrared technique similar to that recently used in the quantum yield determination of *o*-nitrobenzyl derived base photogenerators [5-6], allowed calculation of the percent acid produced in the solid state thermolysis. The C-H deformation at 700 cm^{-1} was taken as a reference band for the polystyrene films, while in a PMMA matrix, the C=O stretch at 1730 cm^{-1} was selected as the reference band with which to gauge the loss of the asymmetric nitro stretch at 1530 cm^{-1}. The ratio (NO_2/ reference band) of the peak area under the nitro absorption and the polymer reference absorption was calculated initially and then again after each heating cycle. The ratio of the amount of *o*-nitrobenzyl tosylate present after heating to the amount present initially multiplied by one hundred gives the percent *o*-nitrobenzyl tosylate remaining after heating (Eq. 3). From this the percent *p*-toluenesulfonic acid formed was found by subtraction (Eq. 2). Thin films taken to 50% decomposition were found to remain unchanged over the period of one week by monitoring the intensity of nitro absorption. This indicates the cleavage is not autocatalytic in acid which is in agreement with the intramolecular mechanism of thermolytic cleavage. Based on this observation, it seems that the amount of acid generated from *o*-nitrobenzyl tosylate may be readily controlled through a combination of temperature and heating time.

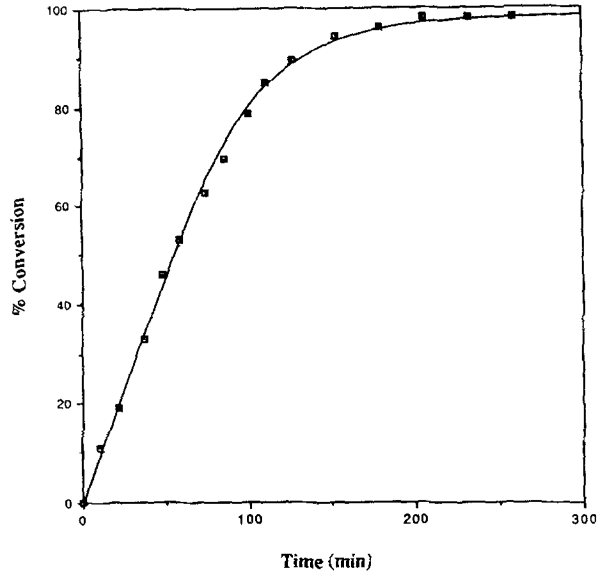


Figure 3. Plot of the % *p*-toluenesulfonic acid generated *versus* heating time for a solution of *o*-nitrobenzyl tosylate at 105°C.

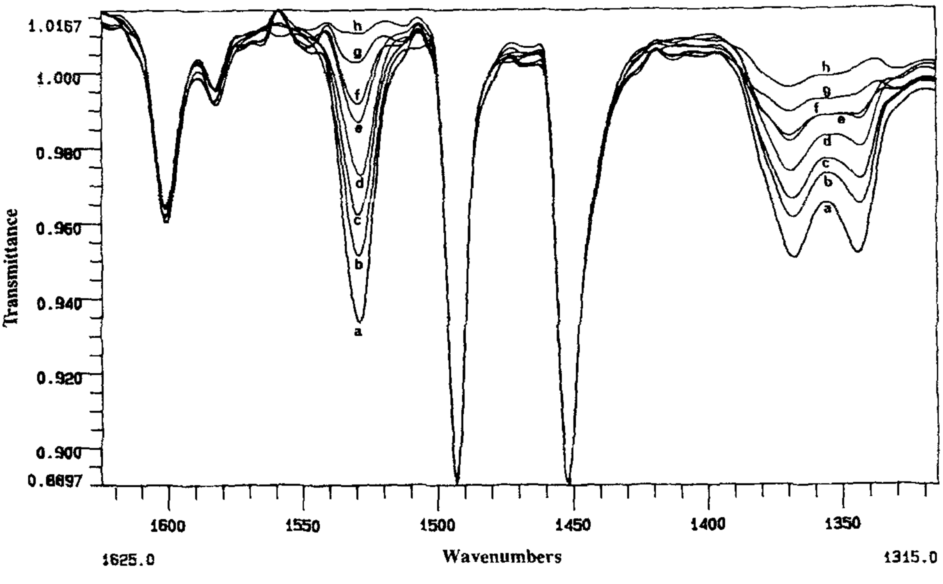


Figure 4: Change in nitro absorption of *o*-nitrobenzyl tosylate in a polystyrene film with increasing heating time at 110°C. a) Prior to heating; b) after 10 min; c) 20 min; d) 30 min; e) 45 min; f) 60 min; g) 120 min; h) 300 min.

This feature indicates *o*-nitrobenzyl tosylate to be well suited to advanced coating applications, where stable pre-polymers are commonly required for processing and molding, prior to final curing. The results of infrared monitoring the thermolysis of *o*-nitrobenzyl tosylate in a polystyrene matrix at 110°C are shown graphically in Fig. 5 and are consistent with the curve derived from the variable temperature ^{1}H NMR solution study (Fig. 3).

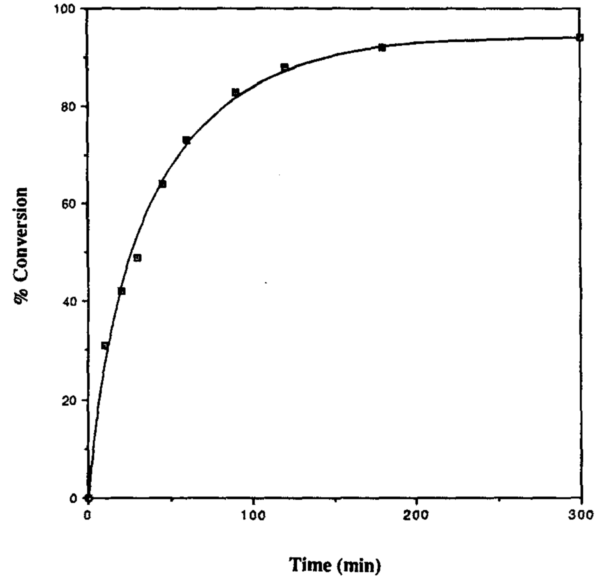


Figure 5. Plot of % *p*-toluenesulfonic acid generated against heating time for *o*-nitrobenzylsulfonate at 110°C in the solid state (polystyrene matrix).

These curves (figure 3 and Figure 5) illustrate the control available for acid generation from *o*-nitrobenzyl tosylate both in solution and the solid state. Furthermore these % conversion curves may be readily used to predict the amount of acid present after a specific heating time which is an important factor in any practical application involving the thermal generation of acid.

$$\%\ \text{Tosylate Remaining After Heating} = \frac{\text{Final (Area NO}_2\text{ Band/ Area Ref Band)}}{\text{Initial (Area NO}_2\text{Band/ Area Ref Band)}} \times \frac{100}{1} \qquad \text{Eq. 3}$$

Conclusions

o-Nitrobenzyl tosylate was found to be an effective source of *p*-toluenesulfonic acid on heating to temperatures above its melting point. At lower temperatures, the thermolytic cleavage was considerably slower although it was still found to occur in the solid state even at 90°C. Direct correlation of the amount of acid generated to the heating time were drawn for both the solution and solid state thermal decomposition of *o*-nitrobenzyl tosylate. Studies on the utility of *o*-nitrobenzyl tosylate as source of thermally generated acid in coatings and in microlithographic applications are forthcoming.

Experimental

o-Nitrobenzyl tosylate was prepared by the method of Houlihan et. al. [3] and found to have spectral properties consistent with its proposed structure. The purity of the material was further determined by elemental analysis: Calculated for $C_{14}H_{13}NO_5S$ (307.31); C 54.71, H 4.26, N 4.56, S 10.43%. Found; C 54.91, H 4.58, N 4.39, S 10.77%. Polystyrene was prepared by standard radical polymerization while PMMA was purchased from Scientific

Polymer Products Inc. Deuteriochloroform, dimethylsulfoxide-d_6 and nitrobenzene-d_5 were purchased from Aldrich.

Infrared spectra were obtained using a Nicolet FT IR/44 spectrometer equipped with software for quantitative analysis. NMR spectra were recorded on a Bruker AF300 Spectrometer using the solvent resonance as standard. DSC was performed using a Mettler DSC30 Low Temperature Cell. TGA was performed on a Mettler TG50 Thermobalance or on a Dupont Instruments Thermobalance. Both Techniques used heating rates of the order 5-10°C/min and purge gases of either air or nitrogen. Microanalysis was performed by M.H.W Laboratories, Phoenix, AZ.

Sample Preparation

The samples used in the quantitative infrared monitoring of thermal acid generation were prepared in the following manner. Polymer (polystyrene or PMMA) (20 wt %) was dissolved in diglyme and 5-10 mol % (relative to polymer) of *o*-nitrobenzyl tosylate added. The resulting solutions were applied to standard silicon, sodium chloride and quartz disks with a Headway Research Spin-coater. All films were dried at 50°C for 30 min and then in vacuo for 12h. Film thicknesses were measured on a Tencor alpha-step and were in the range 0.9-1.1µm.

Acknowledgements.

Financial support of this research by the Office of Naval Research is acknowledged with thanks

References

1. Morrison, H. A. in " The Chemistry of Nitro and Nitroso Groups", Editor, H. Feuer; The Chemistry of Functional Groups Series, Editor, Patai, S.; Part 1, Chapt. 4, p 165, Interscience, 1969: Pillai, V.N.R.; Synthesis, 1980, 1: Zehavi, U.; Adv. Carbohydr. Chem. Biochem., 1988, 46, 179: Pillai, V.N.R. in Org. Photochem., Editor, Padwa, A.; Vol. 9, Chapt. 3, p. 225: Amit, B.; Zehavi, U.; Patchornik, A.; Isr. J. Chem., 1974, 12, 103.
2. Reichmanis, E.; Wilkins, C.W. Jr.; Chandross, E.A.; J. Vac. Sci. Technol., 1981, 19, 1338: Wilkins, C.W. Jr.; Reichmanis E.; Chandross, E.A.; J. Electrochem. Soc., 1982, 129, 2552.
3. Houlihan, F.M.; Shugard, A.; Gooden, R.; Reichmanis, E.; Macromolecules, 1988, 21, 2001.
4. Neenan, T.X.; Houlihan, F.M.; Reichmanis, E.; Kometani, J.M.; Bachman, B.J.; Thompson, L.F.; Macromolecules, 1990, 23, 145.
5. Cameron, J.F.; Fréchet, J.M.J.; J. Am. Chem. Soc., 1991, 113, in press. Cameron, J.F.; Fréchet, J.M.J.; J. Org. Chem., 1990, 55, 5119. Cameron, J.F.; Fréchet, J.M.J.; Proc. Polym. Mat. Sci., 1991, 64, xxx.
6. Beecher, J.E.; Cameron, J.F.; Fréchet, J.M.J.; Proc. Polym. Mat. Sci., 1991, 64, xxx.
7. Gatechair, L.R., Proc. Polym. Mat. Sci., 1988, 59, 289; Gatechair, L.R., Proc. Water Borne and Higher Solids Coat. Symp., 1988, 15, 33.
8. Winkle, W.R.; Graziano,K.A., J. Photopolym. Sci. Technol., 1990, 3, 419.
9. Dickinson, W.B., J. Am. Chem. Soc., 1964, 86, 3580.
10. Ledwith, A., Polymer, 1978, 19, 1217. Crivello, J.V.; Polymer J., 1985, 17, 73.
11. Crivello, J.V.; Lockhart, T.P.; Lee, J.L.; J. Polym. Sci. Polym. Chem. Ed., 1983, 21, 97. Pappas, S.P.; Feng. H.B. in "Cationic polymerization and related processes" (Goethals, E.J., Editor) Academic Press New York 1984, 325. Endo, T.; Uno, H.; J. Polym. Sci. Polym. Chem. Ed., 1985, 23, 359.
12. Sundell, P.E.; Jönsson, S.; Hult, A.; Polym. Mat. Sci. Eng., 1989, 61, 82. Sundell, P.E.; Jönsson, S.; Hult, A. in "Radiation Curing of Polymeric Materials" (Hoyle, C.E., Kinstle, J.F. Editors) Chapter 32, ACS Symposium Series 417, 1990, Washington D.C. Sundell, P.E.; Ph.D. Thesis, Department of Polymer Technology, Royal Institute of Technology, (Prof. A. Hult) Stockholm 1990.

Accepted March 4, 1991 K