Unsaturated Polyester Resins with Different Allyl Ethers as Crosslinking Built-In Monomers

GABRIEL ROKICKI, ELŻBIETA SZYMAŃSKA

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00 664 Warsaw, Poland

ABSTRACT: The effect of the structure of allyl ethers used as built-in monomers of unsaturated polyester resins on the properties of the coatings obtained have been studied. It was found that high hardness of the coatings cured in air using photoinitiators was achieved for the resins with polyfunctional allyl ether monomers incorporated into polyester molecules as the end groups or as the pendant geminal groups. The influence of the presence of a cobalt organic salt on the hardness of the coating from unsaturated resins has also been studied. The extent of crosslinking for the copolymerization of fumaric esters with allyl ethers in air increases, and a smaller amount of photoinitiator may be used when cobalt (II) naphthenate is present in the resin. The results are discussed in terms of the oxidation of allyl ethers and redox cleavage of peroxides formed, leading to an increase in the rate of copolymerization of allyl ethers with fumarate esters. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2031–2039, 1998

Key words: unsaturated polyester resin; allyl ether monomers; ultraviolet photoinitiators

INTRODUCTION

Radical homopolymerization of allyl monomers proceeds with low rate, giving low-molecular-weight products. Because of autoinhibition (the process of hydrogen abstraction from the allyl methyl group, leading to stable radicals), the share of degradative chain transfer to monomer is higher than that of propagation.[1,2] Despite this, allyl monomers are often used in the copolymerization with acceptor monomers (for example, interphase grafting of submicron multilayer particles[3,4]), as well as in the synthesis of unsaturated polyester resins (UPRs).[5,6]

It is well known that in a classical, styrene-containing UPR, the upper layer contacting with air is not completely cured due to oxygen inhibition. It was shown that when β-unsaturated ethers (allyl, methallyl, and crotyl) are present in lacquer compositions, the surface of the resulting film is cured better. β-Unsaturated ethers are easily oxidized at the α-carbon atom, and the resin containing those ethers can be used for air-drying lacquers.[7] The most commonly used allyl ethers are usually added to lacquer compositions as reactive diluents or are incorporated into the polyester chain during polyesterification.[8,9] To achieve good properties of a cured film, at least 3 allyl groups must be present in the polyester molecule, or the content of allyl ether in a lacquer composition should be higher than 40 wt %.[10] Mleziva and coworkers[11,12] studied the autooxidation of different unsaturated compounds and found that, at room temperature, the highest amount of oxygen is absorbed from air by linolenic acid; but in the presence of cobalt salt, the same amount of oxygen is absorbed by glycerol allyl ethers. Compounds with higher electron density at the α-carbon atom absorb a smaller amount of oxygen.

As was shown by Pohl et al.[13] and Traenckener and Pohl[14] for peroxide and photoinitiated copolymerization of allyl ethers with fumaric polyester and styrene in the upper layer of the coating, styrene reacts with allyl groups; but in deeper layers, where no oxygen is present, only copolymerization of styrene with fumaric esters takes place. Johansson and Hult[15,16] have found that allyl ethers have a retarding effect on the polymerization rate when the reaction is performed in the air. The oxidation rate of the allyl ethers decreases when the intramolecular hydrogen bonding to the ether oxygen from hydroxyl groups takes place because of limited resonance stabilization to the ether oxygen. They have shown that the rate of free radical copolymerization of styrene and maleic esters in the presence of allyl ether, performed in air, increased when a cobalt (II) salt was added to the reaction mixture. The accelerating effect is explained by redox cleavage of the peroxides formed, leading to alkoxy radicals, which are more reactive than peroxy radicals.

Fischer and Uerdingen[17] studied the dependence of the extent of crosslinking on the allyl ether content in unsaturated resins and found that, for crosslinking carried out at a high temperature, mainly, copolymerization of allyl monomer with fumaric ester and homopolymerization of the latter takes place. For the resin cured at above 140°C, the allyl monomer content of over 50% of fumaric ester concentration in the resin had no influence on the crosslinking extent.

The aim of our work was to investigate the influence of the structure of allyl ether monomers built into unsaturated polyester chains on the properties of the coatings obtained by photoinduced copolymerization of allyl ethers with fumaric acid esters as the polyester resin reactive groups. Taking into consideration that allyl ethers can be used for oxidative crosslinking of the polyester resin, the influence of a cobalt organic salt on photoinitiated polymerization carried out in air and the properties of the resulting coatings were also studied.

EXPERIMENTAL

Materials

For allyl ethers synthesis, allyl chloride (a product of Chemical Works, ZACHEM, Bydgoszcz, Poland), hexane-1,2,6-triol, trimethylolpropane, cis-2-butene-1,4-diol, pentaerythritol, and methyl ethyl ketone (all products of Aldrich), and propylene oxide and benzaldehyde (both products of Merck) were used without additional purification.

For the synthesis of unsaturated polyester resins fumaric acid and adipic acid (products of Nitrogen Works in Kędzierzyn Koźle, Poland), propane-1,2-diol, monoallyl ether of glycerol (**1**) and triallyl ether of pentaerythritol (**5**) (products of Shell) were used as delivered. For ultraviolet (UV) curing photoinitiators, Irgacure-184 and Irgacure-651 (products of Ciba-Geigy) were used.

Syntheses of Allyl Ethers

Monoallyl ether of trimethylolpropane (**2**), 1-allyloxyhexane-5,6-diol (**3**), and diallyl ether of pentaerythritol (**4**) were prepared according to the previously described method[5] by reaction of a polyhydroxy compound containing, protected, 2 hydroxyl groups with allyl chloride (Scheme 1).

1-Allyloxyhexane-5,6-Diol (3)

The mixture of hexane-1,5,6-triol (120 g, 0.89 mol), ethyl methyl ketone (80 g, 1.11 mol), *p*-toluene sulphonic acid (0.2 g), and heptane (50 mL) was heated at 100–150°C, and the water was removed by azeotropic distillation. The resulting acetal was purified by distillation under reduced pressure, collecting the fraction boiling at 112–115°C (p = 1.5 mmHg). To 116.8 g (0.62 mol) of the acetal, 25.7 g (0.64 mol) of NaOH (pellets) were added, and the mixture was heated to 70°C, then allyl chloride (49.1 g, 0.64 mol) was added dropwise for 30 min, and the reaction mixture was additionally stirred for 2 h. After that, the flask content was neutralized with HCl and extracted with 50 mL of heptane. The organic phase was washed twice with 50 mL of water and, after drying with Na_2SO_4, was purified by distillation under reduced pressure, collecting the fraction boiling at 95–96°C (2.25 mmHg). 75 g (yield 53%) of the product was obtained. To deprotect 2 hydroxyl groups, 20 mL of water and 0.5 g of *p*-toluene sulfonic acid were added, and the reaction mixture was heated under reflux for 1 h. The resulting ethyl methyl ketone was removed by distillation, and the crude 1-allyloxyhexane-5,6-diol was purified by distillation under reduced pressure, collecting the fraction boiling at 105–110°C (p = 0.6–0.8 mmHg). 53.8 g (yield 94%) of **3** was obtained.

^{1}H nuclear magnetic resonance (^{1}H-NMR) (CDCl$_3$): δ (ppm) = 5.78–5.93 (m, H, $=$CH—), 5.12–5.28 (m, 2H,

Scheme 1

=CH$_2$), 4 · 11 (d, 2H =CH—C$\underline{H}_2$—O—) 3.55–3.87 (m, 5H, —CH(OH)CH$_2$OH), 3.34 (s, 2H, =CH—CH$_2$—O—C$\underline{H}_2$—), 1.58–1.71 (m, 6H, CH$_2$). Fourier transform infrared (FTIR) (NaCl): 1415, 1120, and 937 cm^{-1}.

Diallyl Ether of Pentaerythritol (4)

Pentaerythritol (136 g, 1 mol) was dissolved in 1000 mL of hot water containing 5 mL of concentrated HCl. Then, benzaldehyde (106 g, 1 mol) was added dropwise while stirring. The reaction was carried out at room temperature for 5 h, and the reactor content was left for 24 h. After that, the precipitate was filtered off and washed with 100 mL of cold water. The resulting product was crystallized from water, giving 134 g (yield 60%) of monoacetal of pentaerythritol (**I**), mp 131–132°C. To 40 g (0.17 mol) of **I,** 68 g (1.7 mol) of NaOH as a 40 wt % aqueous solution was added, and the mixture was heated to 50°C, then allyl chloride (26 g, 0.36 mol) was added dropwise for 30 min, and the reaction mixture was additionally stirred for 2 h. After that, the reaction mixture was poured into 250 mL of water, and the organic phase was washed twice with 100 mL of water. The product was purified by distillation under reduced pressure, collecting the fraction boiling at 164–167°C (p = 0.8 mmHg). 48 g of

diallyl ether (**II**) was obtained (yield 93%). To deprotect 2 hydroxyl groups, 10 mL of water and 0.63 g of p-toluene sulfonic acid were added to 48 g of **II,** and the reaction mixture was heated under reflux for 1 h. The resulting benzaldehyde was removed of by steam distillation. The crude diallyl ether of pentaerythritol (**III**) was purified by distillation under reduced pressure, collecting the fraction boiling at 122–124°C (p = 0.15 mmHg). 20.5 g (yield 60%) of **III** (**4**) was obtained.

^{1}H-NMR (CDCl$_3$): δ (ppm) = 5.76–5.95 (m, 2H, allylic =CH—), 5.10–5.25 (m, 4H, allylic =CH$_2$), 3.93 (d, 4H =CH—C$\underline{H}_2$—O), 3.71 (m, 4H, CH$_2$—OH), 3.33 (s, 4H, =CH—CH$_2$—O—C$\underline{H}_2$—), 3.25 (m, 2H, OH).

FTIR (NaCl): 1410, 1115, and 943 cm^{-1}.

Monoallyl Ether of Trimethylolpropane (2)

Monoallyl ether of trimethylolpropane was prepared by a similar method to the above one using ethyl methyl ketone instead of benzaldehyde for the protection of 2 hydroxy groups. The crude allyl ether was purified by distillation under reduced pressure, collecting the fraction boiling at 98–101°C (p = 0.8 mmHg; 88% yield).

^{1}H-NMR (CDCl$_3$): δ (ppm) = 5.76–5.95 (m, H, allylic =CH—), 5.10–5.25 (m, 2H, allylic =CH$_2$), 3–93 (d, 2H

Figure 1 Different allyl ether monomers built into unsaturated polyester resin: (**1**) monoallyl ether of glycerol, (**2**) monoallyl ether of trimethylolpropane, (**3**) 1-allyloxy-hexane-5,6-diol, (**4**) diallylether of pentaerythritol, (**5**) triallylether of pentaerythritol, and (**6**) diols with 1,4-dioxy-2-butene group.

=CH—C$\underline{H}_2$—O—), 3.33 (s, 2H, =CH—CH$_2$—O—CH$_2$—), 3.25 (m, 2H, OH), 3.71 (m, 4H, C$\underline{H}_2$—OH), 1.45 (q, 2H CH$_3$—C$\underline{H}_2$—), 0.87 (t, 3H, CH$_3$). FTIR (NaCl): 1412, 1118, and 946 cm^{-1}.

Synthesis of Diol with 1,4-Dioxy-cis-buten-2 Group (6)

To 88 g (1 mol) of *cis*-2-buten-1,4-diol containing 1 mL of BF$_3$ · Et$_2$O cooled to 10–15°C, propylene oxide (174 g, 3 mol) was added dropwise for 2 h, maintaining the reaction temperature below 15°C. After that, the reaction mixture was neutralized with triethylamine, and the product (containing 2 to 3 oxypropylene groups in a molecule) was purified by distillation under reduced pressure, collecting the fraction boiling at 120–145°C ($p = 0.4$–0.6 mmHg).

^{1}H-NMR (CDCl$_3$): δ (ppm) = 5.58–5.70 (m, 2H, —C$\underline{H}$= C$\underline{H}$—), 3.90–4.15 (m, 4H, —O—C$\underline{H}_2$—CH=CH), 3.15–3.45 [m, =CH—CH$_2$—O—C$\underline{H}_2$, =CH—CH$_2$—O—C$\underline{H}$(CH$_3$)—, O—CH$_2$—C$\underline{H}$(CH$_3$)O$\underline{H}$, OCH(CH$_3$)C$\underline{H}_2$O$\underline{H}$], 0.92–1.07 [3d, CH(C$\underline{H}_3$)].

Synthesis of Unsaturated Polyester Resins with Allyl Ether Monomers

146 g (1.26 mol) of fumaric acid, 8.7 g (0.05 mol) of adipic acid, 68.4 g (0.9 mol) of propane-1,2-diol, 97.1 g (0.75 mol) of monoallyl ether of glycerol, 0.05 g of *p*-toluene sulfonic acid as a catalyst, and

Table I   The Characteristics of the Unsaturated Polyester Resin Containing Different Allyl Ether Monomers

Resin	Allyl Groups Content (wt %)	Fumaric Acid Content (wt %)	AV (mg KOH/g)	Viscosity[a] (mPa s)	M_n (g/mol)
1	15.1	47.2	45	5.3	1100
2	15.3	41.5	46	5.8	1150
3	14.8	41.2	44	7.1	1250
4	14.9	46.0	48	4.8	980
5	15.4	48.4	20	4.2	—
6	14.4	36.6	45	5.7	—

For more information, see the experimental section.
[a] Measured at 25°C.

0.5 g of hydroquinone as an inhibitor were placed in a four-necked flask equipped with a mechanical stirrer, condenser, thermometer, and nitrogen inlet. The polycondensation was carried out at a temperature of 170–185°C under an inert gas atmosphere, removing water by distillation assisted by a gas flow. The condensation was proceeded until the acid value (AV) of the resin dropped to 45–47 mg KOH/g.

The resins with other allyl ether monomers were obtained in a similar manner, maintaining almost the same molar ratio of diols to acids (approximately 1.2 : 1) and a similar allyl ether group concentration (approximately 15 wt %). When triallyl ether of pentaerythritol, monofunctional compound with 1 OH group was used as a

crosslinking monomer, the resin synthesis was performed in a different manner. In the first stage, all starting materials except allyl ether were used for polycondensation; and after AV equaled approximately 100 mg KOH/g was achieved, triallyl ether of pentaerythritol was added, and polycondensation was proceeded until the AV of the resin dropped to approximately 20 mg KOH/g.

The UPRs obtained were diluted with butyl acetate to 80 wt % concentration and used for coating preparation.

UV Curing of Unsaturated Polyester Resins

To a UPR butyl acetate solution, a photoinitiator (5 wt %) was added, and films were drawn on glass plates with a 60-μm applicator. The films were cured for 3 to 10 min by UV irradiation in air atmosphere, using a medium-pressure mercury lamp PLK Type 5 (80 W) over the following frequency ranges: 100–280 (maximum 10% absorption), 280–315 (minimum 30% absorption), and 315–380 nm (minimum 50% absorption).

Measurements

The degree of polycondensation was monitored by determination of the AV, the polyester resin viscosity was measured using a rotary viscometer RM-180 Rheomat (Mettler), and a vapor pressure osmometer (Knauer) was used to determine molecular weights. Hardness measurements of the coatings were carried out by means of a König pendulum and were expressed in seconds.

^{1}H-NMR spectra were recorded on a Varian VXR 300 MHz spectrometer using $2 \times 10^{-3}M$ solutions in CDCl$_3$. Chemical shifts are reported

Figure 2 Dependence of the pendulum hardness of the coatings on UV irradiation time for different allyl monomers used for the synthesis of UPRs: (**1**) monoallyl ether of glycerol, (**2**) monoallyl ether of trimethylolpropane, (**3**) 1-allyloxyhexane-5,6-diol, (**4**) diallylether of pentaerythritol, (**5**) triallylether of pentaerythritol, and (**6**) diols with 1,4-dioxy-2-butene group.

Scheme 2

as δ in ppm values relative to $(CH_3)_4Si$ as an internal standard. Infrared (IR) spectra were recorded on a FTIR BIORAD 165 apparatus.

RESULTS AND DISCUSSION

Unsaturated polyester resin containing built-in different allyl ether monomers were obtained and characterized. Allyl ethers were bonded to a polyester chain as pendant groups via the shorter (**1**, **2**) and longer (**3**) spacers, as 2 allyloxymethyl geminal pedant groups (**4**), as tris(allyloxymethyl)methyl end groups (**5**), and as 1,4-dioxy-2-butene groups (**6**) incorporated into the main chain of the polyester (Fig. 1). All the UPRs contained almost the same amount (approximately 15 wt %) of allyl ether groups independently of the chemical structure of the monomer used. As was shown earlier,[6] the resins with higher con-

centration of allyl ether groups were unstable during synthesis and storage in air atmosphere.

Since both the unsaturated polyester and crosslinking monomer were present in the reaction mixture during polycondensation, a greater amount of the inhibitor (up to 0.2 wt % of hydroquinone) than that used for classical UPR had to be added, and the reaction was carried out at a temperature lower than 190°C to avoid uncontrolled polymerization during the resin synthesis. The molar ratio of diols to dicarboxylic acids used was approximately 1.2 to 1. When a lower ratio was applied, the risk of resin gelling during synthesis was much higher. To compare the resins' reactivity and properties of the resulting coatings, all the resins obtained had a similar molecular weight (M_n) of approximately 1100 (AV = 45–47 mg KOH/g; for **5** AV = approximately 20 mg KOH/g). The characteristics of the resins obtained are presented in Table I.

Scheme 3

In Figure 2, the dependence of hardness of the coatings obtained from UPR containing different allyl ether monomers on time of UV irradiation is shown. The presence of fumarate esters in the resin enables fast reaction with allyl radical in comparison with homopolymerization of allyl ether monomers. The ability of fumarate monomer radical (a conjugated one) to abstract an allylic hydrogen is small, and the chain transfer reaction, which is characteristic of allyl polymerization and is essentially a termination reaction, is reduced when a high mole fraction of fumarate ester in the monomer feed is present [eq. (2) in Scheme 2].[18] The highest pendulum hardness was observed for coatings from the resin based on triallyl ether of pentaerythritol incorporated into polyester as the end groups (curve **5**) and the coatings containing diallyl ether of pentaerythritol (2 geminal pendant allyl groups in the chain) (curve **4**) had a slightly lower hardness. The high hardness of those coatings is due to the vicinity of allyl groups and because of the higher reactivity of the less-hindered end groups. An increase in the allyl functionality leads to acceleration of oxidation due to intramolecular hydrogen abstraction,[15,16] and, as a consequence, the share of oxidative crosslinking is higher. Almost the same hardness, but lower than that of the previously

mentioned one, was observed for coatings from monoallyl ether of glycerol and trimethylolpropane (Fig. 1, curves **1** and **2**). In the case of the coating containing allyl ether groups bonded to the polyester chain via a longer spacer, a lower hardness is probably caused by the internal plastification effect of the long aliphatic pendant groups (curve **3**).

The poorest properties were observed for coatings from the resin with 1,4-dioxy-2-butene groups incorporated as part of the polyester chain (curve **6**). Due to the steric hindrance of 1,2-substituents and the presence of 2 oxygen atoms near the double bond, the reactivity of such monomers was much lower than that of the monosubstituted vinyl monomer, and the resulting crosslinking density decreased. For that resin, because of the high molecular weight of diol used, the fumarate ester content was also lower.

For curing of the UPRs, 2 photoinitiators based on acetophenones (1-hydroxycyclohexylphenyl ketone (Irgacure 184) and α,α'-dimethoxy-α-phenylacetophenone (Irgacure 651) were used.

The above-mentioned photoinitiators undergo a rapid α-cleavage (Norrish type I) from their excited triplet state.[19,20] The subsequent photochemical transformation of the resulting radicals pair, however, is quite different. The 1,1-dimethoxybenzyl radical from Irgacure 651 undergoes a secondary fragmentation reaction to yield the inactive methyl benzoate and the active methyl radical (Scheme 3). In the case of Irgacure 184, hydrogen transfer within the radical pair is the major process. It is known that benzoyl radical generated from Irgacure 651 is efficiently quenched by oxygen. The quantum yields of the photoreactions of Irgacure 651 are higher in the presence of oxygen, indicating that oxygen and

Table II   Influence of the Kind of Photoinitiator and Time of UV Radiation on Pendulum Hardness of Allyl UPR Coatings

Photoinitiator	Pendulum Hardness (in s) for Different Times of UV Radiation			
	4 min	6 min	8 min	10 min
Irgacure 651	52 (63)[a]	74	96	98
Irgacure 184	53 (65)[a]	84	108	111

Resin was obtained using triallyl ether of pentaerythritol as a crosslinking monomer.
[a] Pendulum hardness after 72 h of exposition in air of a partially cured coating.

Table III The Influence of Cobalt Naphthenate Content on the Pendulum Hardnessof UV-Cured UPR Coatings

Content of Co Naphthenate (wt %)	Pendulum Hardness (in s) After UV Radiation				
	3 min	5 min	6 min	8 min	10 min
Irgacure 184 (4 wt %):					
0	14	22	46	60	77
0.03	14	23	50	63	80
0.06	17	31	57	74	83
0.09	23	42	67	82	84
Irgacure 184 (5 wt %)					
0	15	57	84	108	111
0.03	18	56	75	96	110
0.06	46	75	90	108	112
0.09	74	85	105	110	112

Resin was obtained using triallyl ether of pentaerythritol as a crosslinking monomer.

the resulting benzoyloxyl radical interact with the radicals of Irgacure 651 in their solvent cage. On the other hand, the quantum yields of Irgacure 184 and the yield of cyclohexanone are unaffected by oxygen, indicating that oxygen cannot interfere with the primary cage reactions of radicals generated from Irgacure 184.[21] It was observed that in air atmosphere when the Irgacure 184 was used crosslinking density of the resins cured was the highest one. The pendulum hardness for Irgacure 184 was 108 s, while for Irgacure 651 was 96 s.

It was also noticed that the hardness of the incompletely cured polyester coatings increase when they are exposed to air (Table II). This is caused, as was shown by Solomon,[22] by the oxidative crosslinking via peroxide groups [eq. (1) in Scheme 2]. Taking the above into consideration, the influence of cobalt (II) naphthenate on the hardness of coatings cured with a photoinitiator (Irgacure 184) in the air was studied. The results presented in Table III show that when a cobalt salt was added, high pendulum hardness of the coatings was attained in a shorter time of UV irradiation than that for the photoinitiator used

alone. In the presence of a cobalt salt, the same pendulum hardness was achieved for a smaller amount of photoinitiator. This accelerating effect of Co naphthenate can be explained by a redox cleavage of peroxides formed (both hydroperoxide from the resin and perbenzoic acid from the photoinitiator), leading to an increase in the rate of copolymerization of allyl ethers with fumarate esters (Schemes 2 and 4).

CONCLUSIONS

High hardness of the coatings cured in air using photoinitiators can be achieved for a unsaturated polyester resin with polyfunctional allyl ether monomers incorporated into polyester molecules as the end groups or as the pendant geminal groups. The extent of crosslinking for copolymerization of fumarate esters with allyl ethers in air increases, and a smaller amount of photoinitiator may be used to get high pendulum hardness of the coatings, when cobalt (II) naphthenate is present in the resin.

Scheme 4

REFERENCES

1. P. D. Bartlett and F. A. Tate, *J. Am. Chem. Soc.,* **75,** 91 (1953).
2. G. Odian, *Principles of Polymerization,* 2nd ed., Wiley-Interscience, New York, 1981, p. 250.
3. U.S. Pat. 4,139,692 (1979).

4. U.S. Pat. 4,263,417 (1981).
5. E. Szymańska, M. Sapieja, and G. Rokicki, *Polimery,* **38,** 393 (1993).
6. G. Rokicki, *Polimery,* **40,** 630 (1995).
7. G. Rokicki, Z. Florjańczyk, L. Ľukasik, and Z. Žukowska, *J. Macromol. Sci., Pure Appl. Chem.,* **A33,** 505 (1996).
8. U.K. Pat. 887,394 (1962).
9. U.K. Pat. 1,013,621 (1965).
10. V. F. Jenkins, A. Mott, and J. R. Wicher, *J. Oil Colour, Chem. Assoc.,* **44,** 42 (1961).
11. J. Mleziva and J. Janušek, *Deutsch. Farben Ztg.,* **21,** 119 (1967).
12. J. Klaban, J. Vlaček, and J. Mleziva, *J. Polym. Sci.,* **16,** 247 (1967).
13. U. H. Pohl, H. J. Traenckener, and H. J. Rosenkranz, *Angew. Makromol. Chem.,* **98,** 1 (1981).
14. H. J. Traenckener and H. U. Pohl, *Angew. Makromol. Chem.,* **108,** 61 (1982).
15. M. Johansson and A. Hult, *J. Polym. Sci., Part A: Polym. Chem.,* **29,** 9 (1991).
16. M. Johansson and A. Hult, *J. Polym. Sci., Part A: Polym. Chem.,* **29,** 1639 (1991).
17. W. Fischer and K. Uerdingen, *Farbe U. Lack.,* **97,** 962 (1992).
18. A. Matsumoto, H. Kamigaki, and M. Oiwa, *J. Polym. Sci., Polym. Chem. Ed.,* **20,** 2611 (1982).
19. J. P. Fouassier and A. Merlin, *J. Photochem.,* **12,** 17 (1980).
20. G. Kornis and P. de Mayo, *Can. J. Chem.,* **42,** 2822 (1964).
21. X. T. Phan, *J. Rad. Curing,* **13**, 11 (1986).
22. D. H. Solomon, *The Chemistry of Organic Film Formers,* R. E. Krieger Publishing, New York, 1977, p. 149.