Photobase-Generating New Polyurethanes with Oxime–Urethane Groups in the Main Chain

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ABSTRACT: New polymeric photobase generators containing oxime–urethane groups were prepared by the polyaddition reaction of 2,4-tolylene diisocyanate with terephthalaldehyde dioxime in the presence or absence of a polyol component to study the ability of these polymers to generate amines through the photolysis of oxime–urethane linkage. The amines induced the crosslinking of poly(glycidyl methacrylate), as proved by the variation of the amount of the insoluble fraction of polymer films with the heating temperature and/or irradiation time. UV and IR absorption spectra indicated that the thermal crosslinking of poly(glycidyl methacrylate) was catalyzed by the photogenerated amines. The photobehavior of the polymers was followed by a reduction of the absorption band at 290 nm, which was characteristic of oxime–urethane groups, as a function of the UV irradiation time. Blue fluorescence was visualized by the treatment of irradiated films with fluorescamine. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2324–2332, 2004

Key words: polyurethanes; oxime-urethane; photobase generating; irradiation; UV-vis spectroscopy

INTRODUCTION

Ionic photoinitiators continue to be the subject of numerous articles because of the wide range of practical applications in microlithography, photoresists, coatings, and so forth. Of real interest are anionic photoinitiators, whose ability to generate bases by the photolysis of some specific groups has been exploited in developing advanced industrial technologies. To efficiently form free amines under the exposure conditions commonly used in the photoimaging industry, a high absorption of the photoinitiator in the near-UV region and a high catalytic activity of the base during the thermal curing reaction are required.[1] Photobase generators have been successfully used as photochemical crosslinking agents for epoxy resins,[2,3] positive-type photoresists,[4,5] base-catalyzed chemically amplified photoresists,[6] imidation catalysts for poly(amic esters)[7,8] and polyisoimide,[9] and surface modification.[10,11] Among them, oxime–urethane derivatives have been studied to produce amines photochemically able to catalyze the thermal crosslinking of epoxy resins.[12,13] Thus, glycidyl methacrylate copolymers with *o*-acyloxyimine or benzophenoneoxime allyl urethane moieties were anionically photocrosslinked with pendant amines produced through the photolysis of oxime–urethane groups.[14,15] Other photobase generators, such as benzophenone oxime *N*-cyclohexylurethane and dibenzophenone oxime *N,N*-hexamethylenediurethane, efficiently induced the crosslinking of poly(glycidyl methacrylate) (PGMA) upon heating.[12] A similar reaction was also investigated to modify the hydrophilicity of epoxy copolymers with oxime–urethane and *N*-substituted maleinimide polymerizable groups.[14]

This article reports on the synthesis, properties, and photochemistry of new polyurethanes with oxime–urethane groups incorporated by means of terephthalaldehyde dioxime (M) and examines their ability to generate bases that can be further used in curing reactions of PGMA.

EXPERIMENTAL

Monomer synthesis

M

Terephthalaldehyde (9 g, 67.2 mmol) was dissolved in 40 mL of ethanol, and HCl · H_2N—OH (10.3 g, 148 mmol) was added dropwise under continuous stirring at 5°C until the solution became clear. The mixture was then refluxed for 1 h and allowed to cool at room temperature. The aqueous layer was extracted twice with diethyl ether, and the combined layers were dried on Na_2SO_4. The solvent was evaporated under reduced pressure to produce a white powder (9.65 g, mp = 199°C, yield = 87.6%).

^{1}H-NMR [dimethyl sulfoxide (DMSO-d_6), δ ppm]: 3.45 (2H, s, OH), 7.35 (4H, s, 1,4-phenylene), 7.9 (2H, s, CH═N). IR (cm^{-1}): 3200 (OH), 2800 (CH), 1630

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(CH═N). ANAL. Calcd for T_1 ($C_8H_8N_2O_2$): C, 58.54%; H, 4.88%; N, 17.07%. Found: C, 58.50%; H, 4.87%; N, 16.95%.

Model compound terephthalaldehyde-bis(phenylcarbamoyloxy)dioxime (M_1)

M (1.148 g, 7 mmol) dissolved in 20 mL of anhydrous dimethylformamide (DMF) was reacted with phenylisocyanate (1.666 g, 14 mmol) at 60°C for 7 h under an argon atmosphere. The cooled solution was concentrated *in vacuo*, and the solid residue was recrystallized from CH_3OH, giving rise to a white solid (2.66 g, yield = 95.0%).

^{1}H-NMR (DMSO-d_6, δ ppm): 8.35 (2H, s, CH═N), 7.2 (4H, s, 1,4-phenylene), 7.1 (10H, m, phenyl). IR (cm^{-1}): 3350 (free NHCOO), 3300 (H-bonded NHCOO), 1670 (H-bonded CO), 1610 (CH═N), 1515 (amide I), 1460 (amide II). UV (DMF): λ_{max} = 256 nm. ANAL. Calcd for M ($C_{22}H_{18}N_4O_4$): C, 65.67%; H, 4.47%; N, 13.9%. Found: C, 65.63%; H, 4.44%; N, 13.78%.

Polymer synthesis

The polyurethane sample PU-1, containing oxime–urethane groups, was obtained by a prepolymer technique through the reaction of 0.01 mol of dehydrated poly(tetramethylene oxide) (PTMO) diol (with an average molecular weight of 2000) with 0.03 mol of tolylene diisocyanate (TDI; an 80:20 v/v 2,4/2,6-isomer mixture) at 65°C for 4 h under purified nitrogen. The resulting prepolymer, end-capped with isocyanate groups, was subsequently chain-extended with 0.02 mol of M in anhydrous DMF (concentration = 20 g dL^{-1}) at the same temperature for 4 h (1:3:2 molar ratio of the reactants). A second polymer (PU-2) was prepared under the same conditions, with the molar ratio (2:3:1) between the partners varied. A third polymer (PU-3) with a high concentrations of hard segments based on TDI (0.01 mol) and a stoichiometric amount of terephthalaldehyde was prepared in a DMF solution (concentration = 20 g dL^{-1}) at 65°C for 12 h under purified nitrogen. The evolution of these reactions was followed by IR spectroscopy up to the disappearance of the hydroxyl and NCO groups, the stretching bands of which were located at 3480 or 3200 cm^{-1} and 2260 cm^{-1}, respectively. All the polymers were precipitated in methanol and dried for 48 h at 60°C under reduced pressure.

PU-1 and PU-2

^{1}H-NMR (DMSO-d_6, δ ppm): 1.45 (protons of the CH_2—CH_2 group from PTMO), 2.25 (protons of the CH_3 group from TDI), 3.35 (protons of the CH_2—O group from PTMO), 4.05 (protons of the CH_2OCONH group), 7.0 and 7.7 (protons of the aromatic ring from TDI), 7.55 (protons of the 1,4-phenylene ring), 8.05 (protons of the CH═N group).

PU-3

^{1}H-NMR (DMSO-d_6, δ ppm): 2.25 (CH_3 protons from TDI), 7.4 (protons of the 1,4-phenylene ring), 7.0 and 7.7 (aromatic protons from TDI), 7.9 (protons of the CH═N group). UV (DMF): λ_{max} = 290 nm.

Insoluble fractions

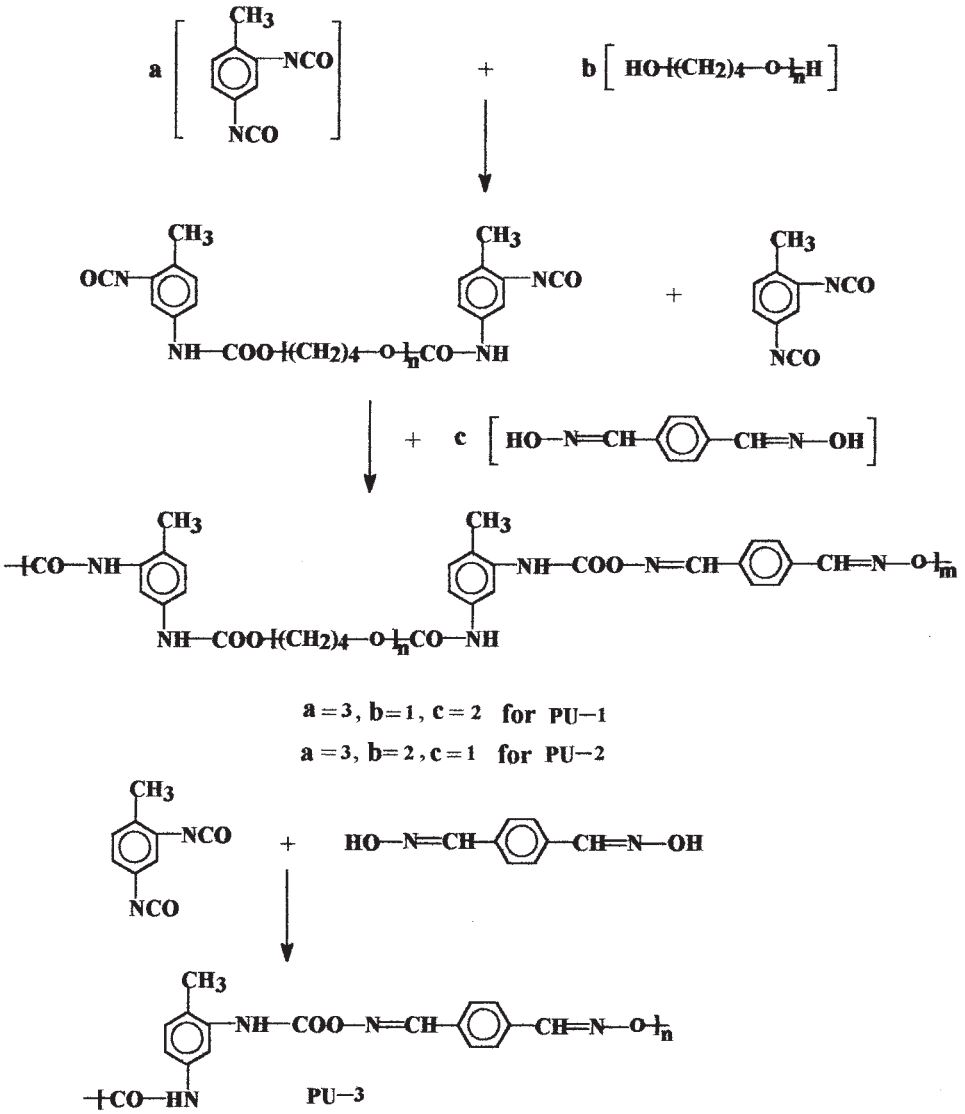
PGMA had an average molecular weight of 18,000 and a polydispersity index of 1.51. Clear and transparent films of PGMA containing 1 wt % PU-1 or PU-3 or 5% M_1 (the model compound) were obtained via the casting, onto quartz plates, of mixtures (1:1 v/v) of PGMA solutions in tetrahydrofuran (THF; 5%) and DMF solutions containing PU-1 or PU-3 (0.5%) or M_1 (2.5%). The films were vacuum-dried at room temperature for 24 h, and the absorbance of the sample under study in the absorption band maximum was kept between 0.7 and 0.8. The coated plates were UV-irradiated (the light being generated by a high-pressure Hg lamp) for different periods of time under a nitrogen atmosphere and then were immersed in THF for 4 min. The insoluble fractions in the irradiated and heated films or only in the ones heated for different periods were also measured. The insoluble fraction of each polymer film was determined as follows:

$$\text{Insoluble fraction (\%)} = (W_3 - W_1)/(W_2 - W_1) \times 100 \quad (1)$$

where W_1 is the weight of the uncoated plate, W_2 is the weight of the coated plate, and W_3 is the weight of the coated plate after curing and development (drying under reduced pressure).

Characterization

The structures of the monomers and polymers were verified by ^{1}H-NMR, IR (Jena, Germany), and UV (Jena, Germany) spectroscopy with JEOL 60-MHz, Specord M80, and Specord M42 spectrophotometers, respectively. The thermal transition temperatures were determined with differential scanning calorimetry (DSC; DSC 12 E, Mettler). The thermal analysis of the polyurethanes was carried out on a derivatograph (MOM, Budapest, Hungary). Thermogravimetry (TG) and thermal gravimetric analysis (TGA) curves were recorded in air between 20 and 600°C at a heating rate of 12°C·min^{-1}. DSC (Greifensee, Switzerland) analysis from 50 to 350°C was recorded with a differential scanning calorimeter (PerkinElmer) at a heating rate of 5°C·min^{-1}. The weight of each sample was 10 mg. The reduced viscosity of the polyurethanes was measured



Scheme 1 Synthesis of polyurethanes with oxime–urethane units.

in DMF (concentration = 0.3 g · dL^{-1}, temperature = 25 ± 0.2°C) with an Ubbelohde viscometer.

RESULTS AND DISCUSSION

As a monomer, M was prepared through the condensation of terephthalaldehyde and hydroxylamine. The elemental and spectral analysis data (^{1}H-NMR, IR, and UV) given in the Experimental section were consistent with the calculated values and corresponded to the assigned chemical structure. Polyurethanes with oxime–urethane groups were synthesized from M, which was used as a partner in the two-step addition reaction between PTMO, TDI, and the aforementioned derivative in a 1:3:2 (PU-1) or 2:3:1 (PU-2) molar ratio with a hard-segment concentration of 31 or 16.1%, respectively (Scheme 1).

Such polymers are block copolymers with long soft segments including the polyether component and short hard segments containing urethane structures and oxime–urethane units inserted into the polyurethane backbone. One hard polyurethane (PU-3) based on TDI and M was prepared too. The main difference in the resulting polymers was structural and may be related to the presence of flexible segments in PU-1 and PU-2 and consequently to the different amounts of M (PU-1, 11.5 wt %; PU-2, 3.5 wt %; and PU-3, 44.5 wt %) in the polymer chains. All the polymers exhibited good solubility in DMF, dimethylacetamide, and THF. The codes of the polymers, reduced viscosities, molecular weights, and polydispersities are given in Table I.

The structures of all the polymers were determined with elemental analysis, IR and ^{1}H-NMR spectroscopy, viscosity measurements, and DSC and TG tech-

TABLE I
Characteristics of Polyurethanes with Oxime–Urethane Groups

Polymer	M_w	M_w/M_n	η_{red} (g/dL[f])	C (%)		H (%)		N (%)	
				Calcd	Found	Calcd	Found	Calcd	Found
PU-1	19900	1.18	0.16	65.34	65.23	10.03	9.98	2.39	2.33
PU-2	41100	1.33	0.284	23.05	59.87	10.04	8.54	2.39	2.46
PU-3	5800	1.10	—	60.35	60.26	4.14	4.10	16.56	16.38

M_w = weight-average molecular weight; M_n = number-average molecular weight; η_{red} = reduced viscosity.

niques. The elemental analysis data agreed with the calculated data, confirming the expected structures. The ^{1}H-NMR spectra of the polymers, together with the assignments of the observed resonances, revealed a singlet at 7.9–8.05 ppm, which was characteristic of the proton in the azomethine units, and a multiplet at 7.0–7.7, which was attributed to the hydrogen atoms in the aromatic ring. The IR spectral analysis of the polymers was performed on solvent-cast thin films. Characteristic absorption bands due to N—H stretching at about 3400 (non-hydrogen-bonded vibration) and 3310 cm^{-1} (hydrogen-bonded vibration), the C—H vibration in the 2880–2970-cm^{-1} region, the CH═N vibration at 1610–1630 cm^{-1}, the C═O stretching vibration at 1730 (non-hydrogen-bonded vibration) and 1710 cm^{-1} (hydrogen-bonded vibration), and that of the Ar ring at about 1600 cm^{-1} for all the films could be identified. Additionally, PU-1 and PU-2 showed absorption bands at 1125 and 2880 cm^{-1}, which were attributed to the C—O—C group from PTMO and the CH group, respectively.

The DSC investigation of the aforementioned polyurethanes gave insight into the morphological structures of these polymers. The thermogram of PU-1 [Fig. 1(a)] shows three endotherms at −16.8, 57.58, and 244.69°C. Commercial polyurethanes generally display a soft-segment glass-transition temperature (T_g) around −30°C, followed by a series of melting endotherms for semicrystalline hard segments.[16] The variation of T_g of the soft segment as a function of the composition and chemical structure can be used as an indicator of the degree of microphase separation. Therefore, the increase in the soft-segment T_g for the studied system at −16.8°C may be attributed to a certain extent of solubilization of the hard segments into the continuous phase of soft segments (phase mixing) caused by the interference of the hard-segment unit in the hydrogen-bonding process. The peak at 57.58°C probably resulted from the dissociation temperature of the hard-segment short-range order, whereas the last endotherm indicates the melting of the hard segments. Additionally, two broad exotherms at 165.2 and 290°C were observed. The first was associated with the deblocking reaction of oxime–urethane moieties followed by thermally induced crosslinking of these groups present along the polymeric backbone, and the second one was attributed to thermal degradation. Unlike PU-1, PU-3 [Fig. 1(b)] displayed one endothermic peak (68.92°C) and two exothermic peaks (171.83 and 255.75°C). In fact, an increase in the hard-segment content was followed by an increase in the peak temperature of the hard-segment melting endotherm and by a reduction of the decomposition temperature of the pure hard polymer.

In the TG curves of the polymers (Table II), the weight loss occurred in three well-defined steps. Because of the decomposition of oxime–urethane moieties, the first stage of the thermal process started at 130 (PU-3), 150 (PU-2), or 180°C (PU-1). As these data show, with increasing oxime–urethane content, the polymer stability was affected in accordance with the aforementioned description of the DSC thermograms. Consequently, the thermal decomposition temperature, defined as the temperature of 10% weight loss, was higher for the polymers with polyether segments in the main backbone.

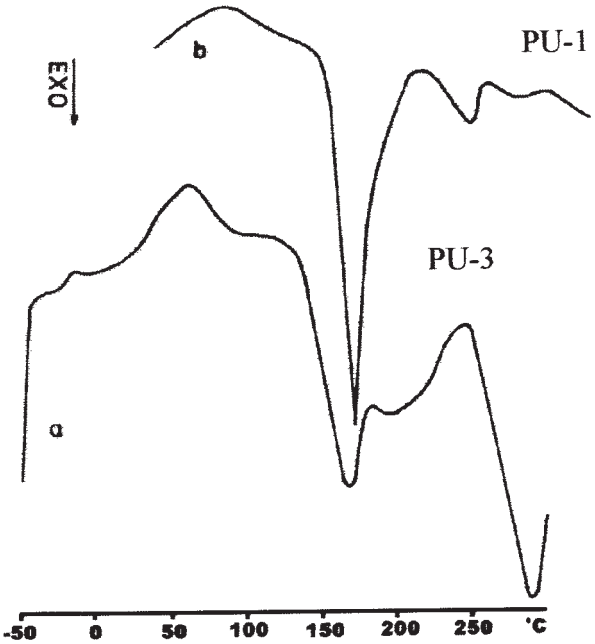


Figure 1 DSC thermograms of (a) PU-1 and (b) PU-3.

TABLE II
Thermal Behavior of Oxime–urethane Polymers

	Stage I				Stage II				Stage III	
Sample	$T_i - T_f$ (°C)	T_{max} (°C)	$T_{10\%}$ (°C)	Weight loss (%)	$T_i - T_f$ (°C)	T_{max} (°C)	$T_{10\%}$ (°C)	Weight Loss (%)	$T_i - T_f$ (°C)	Weight loss (%)
PU-1	180–260	240	—	6	260–310	300	300	5	310–480	74
PU-2	150–300	270	—	8	300–450	420	335	69	450–570	26
PU-3	130–200	180	170	20	200–350	220	—	25	350–520	10

T_i = temperature of initial decomposition from the thermogravimetric curve (TG); T_f = temperature of final decomposition from the TG curve; T_{max} = temperature of the maximum rate of weight loss from the TG curve; $T_{10\%}$ = temperature of 10% weight loss from the TG curve.

Photochemical behavior

To observe the photobehavior of the oxime–urethane structure, we conducted UV photolysis experiments on the synthesized model. Upon the irradiation of the model compound in methanol with 365-nm UV light, the absorption band around 256 nm, assigned to a π–π^* transition, decreased gradually with the irradiation time [Fig. 2(a)]. The presence of isosbestic points at 238 and 272 nm was observed too. This result provided evidence that the photodecomposition of the oxime–urethane unit (75% transformation degree) in methanol occurred in time (ca. 20 min) concomitantly with the appearance of a new maximum at 304 nm, which was attributed to the azine-type structure formation.[12,15] The photolysis process can be expressed by a first-order rate equation: $\ln(A_0 - A_\infty)/(A_t - A_\infty) = kt$, where A_0, A_∞, and A_t are the absorbance at times t_0, t_∞, and t, respectively, and k is the rate constant [Fig. 2(b)]. In fact, the photolysis constant rate for the oxime–urethane model ($k = 2.08 \times 10^{-3}$ s^{-1}) was probably affected by the solvent nature, but the linearity of the first-order plot suggests that the microenvironments around the photocleavable groups were uniform.

A comparison of the model solution spectrum with that of polymer PU-1 in DMF indicated a bathochromic shift of the π–π^* transition characteristic of oxime–urethane units, with a slight reduction of the absorption band centered at 290 nm when an isosbestic point at 330 nm appeared in the spectrum. More specifically, UV light stimulated the appearance of new structures around 370 nm, and the phototransformation of oxime–urethane groups at equilibrium (ca. 45%) needed only 5 min [Fig. 3(a)]. Therefore, one direct result of the irradiation of oxime–urethane groups was the formation of azine-type derivatives characterized by absorptions at 370 nm as a result of extended conjugation. The evolution of the photoprocess could be considered a two-step process exhibited with different rates. The first step (for about 75% of the photoprocess) had a rate constant of 7.72×10^{-2} s^{-1}, whereas the second one was slower [Fig. 3(b)].

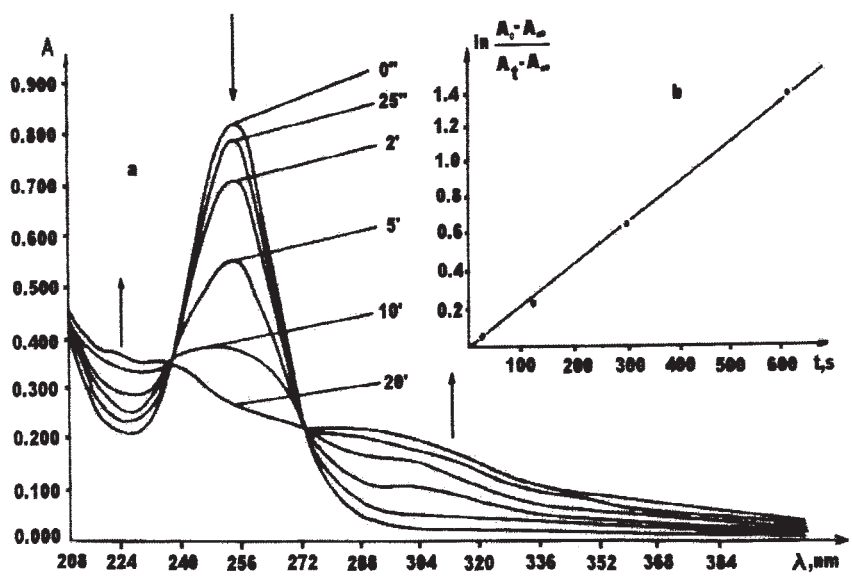


Figure 2 (a) Changes in the UV–vis absorption spectra of the phenylurethane–dioxime model compound (M_1) in a methanol solution upon UV light exposure of 365 nm and (b) a kinetic profile.

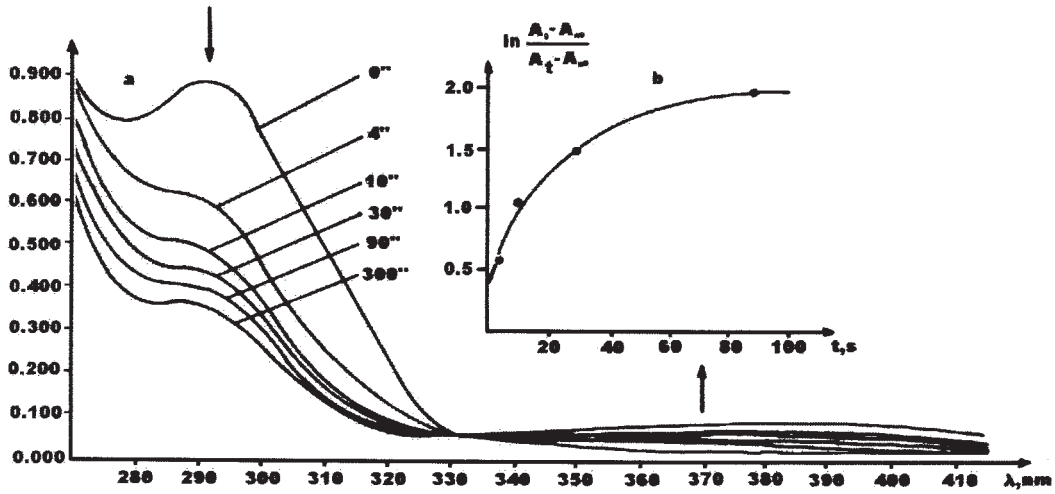
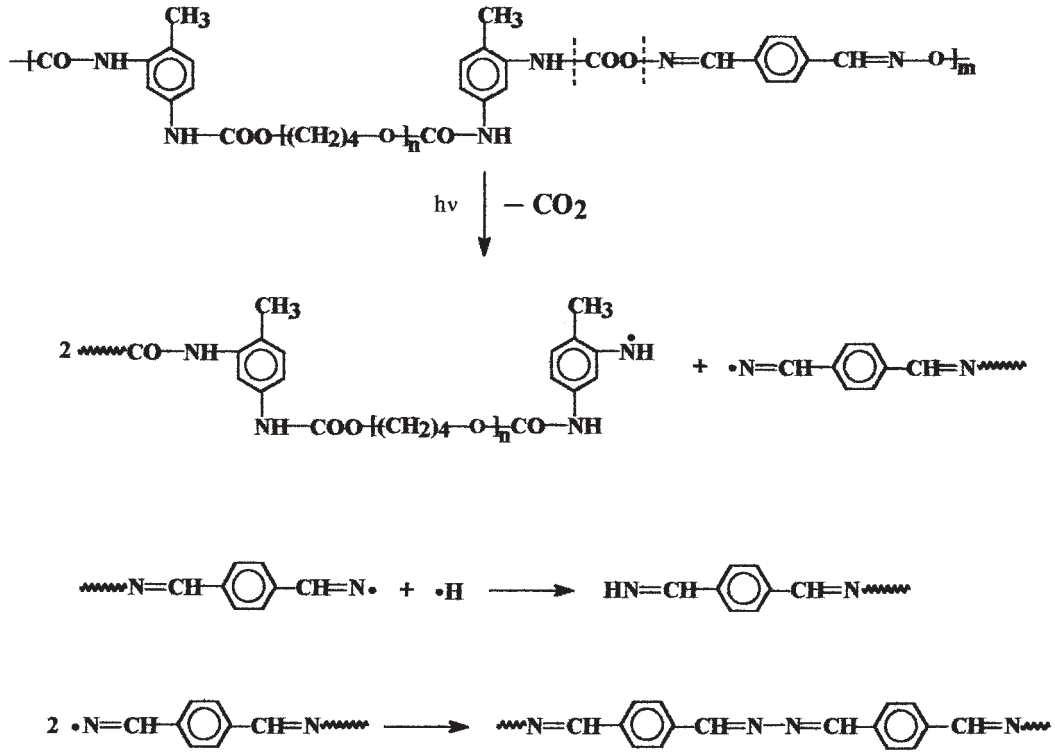


Figure 3 (a) Changes in the electronic absorption spectra of PU-1 in a DMF solution upon UV irradiation at 25°C and (b) a kinetic plot. The irradiation times are indicated.

Scheme 2 presents some possible reactions explaining how the polyurethane with oxime–urethane groups could function as a photobase-generating polymer. Upon the exposure of polymers to UV light, a homolytic cleavage of the N—O bond with the formation of an iminyl–carbamoyloxy radical pair is induced. The former radical undergoes hydrogen abstraction or dimerization leading to an imine or azine structure, respectively. The carbamoyloxy radical can form an aminyl radical through a decarboxylation reaction accompanied by hydrogen abstraction to produce polymers with amine groups. At first glance, the formation of such photolysis intermediates seems to play the main role in the development of photosensitive polymers.

An important indicator of polymeric backbone photosensitivity could be the modification of the reduced viscosity of the polymers with the irradiation time



Scheme 2 Photodecomposition mechanism for oxime–urethane polymers.

TABLE III
Variation of the Reduced Viscosity (η_{red}) for Oxime–Urethane Polyurethanes with the Irradiation Time

Sample	η_{red} (g/dL) for an irradiation time (h) of			
	Initial	3	6	11
PU-1	0.16	0.25	0.21	0.18
PU-2	0.29	0.32	0.32	0.30

TABLE IV
Effect of Heating Time on the Insoluble Fraction of PGMA Films with PU-1 (1%) or M_1 (5%)

Sample	Insoluble fraction (%)							
	100°C				60°C			
	5 min	10 min	15 min	20 min	5 min	10 min	15 min	20 min
PGMA/PU-1	14	47	57	72	4	8	31	43
PGMA/M_1	4	9	22	23	7	8	10	19

(Table III). An increase in the reduced viscosity of polymer solutions after 3 h of irradiation (PU-1, 0.25 g dL^{-1}, and PU-2, 0.32 g dL^{-1}), in comparison with the nonirradiated parent samples (0.16 and 0.29 g dL^{-1}), may be interpreted in terms of the crosslinking effect. The exhaustive irradiation of these polymers for 11 h caused a decrease in the reduced viscosity (PU-1, 0.18 g dL^{-1}, and PU-2, 0.30 g dL^{-1}) because of bond cleavage of the polymer backbone.

Additional characteristics of the photoprocess were obtained from the IR spectroscopy data, visible differences between the original and final structures of the polymer films being expected. Figure 4 shows the IR absorption spectral changes of the PU-1 film as a function of the irradiation time. Indeed, in the film irradiated for 6 h, an intense reduction of the hydrogen-bonded carbonyl groups was observed because of the photodecomposition of oxime–urethane units followed by a decarboxylation reaction. Consequently, the slight increase in the free carbonyl groups could be attributed to the photooxidation of the polymer. Therefore, it seems reasonable to assume that the appearance of amine, typical of the photodecomposition of oxime–urethane structures, was mainly responsible for all the observed spectral modifications.

To prove that the amine generated from the photolysis of these groups inserted into the polyurethane chain could initiate curing reactions of polymers possessing glycidyl groups, films of PGMA containing small amounts of oxime–urethane polymers or the model compound were heated, irradiated, and irradiated and heated. The solubility changes of the polymers were followed through the insoluble fractions. Table IV summarizes the effect of the heating time on the thermal crosslinking of PGMA films with either PU-1 (1 wt % in THF) or M_1 (5 wt % in THF). Thus, upon heating, the insoluble fraction of the PGMA/PU-1 film significantly increased from 14 up to 72% at 100°C and from 4 to 43% at 60°C. For the model compound (M_1) incorporated into the PGMA film, the increase was lower than 25% at 100°C. In the absence of PU-1 or M_1, PGMA films were not crosslinked up to 120°C. Moreover, the thermal stability of the polymers with oxime–urethane moieties and PGMA (Table IV) suggested that the epoxy groups could react directly with the blocked isocyanate units.[17]

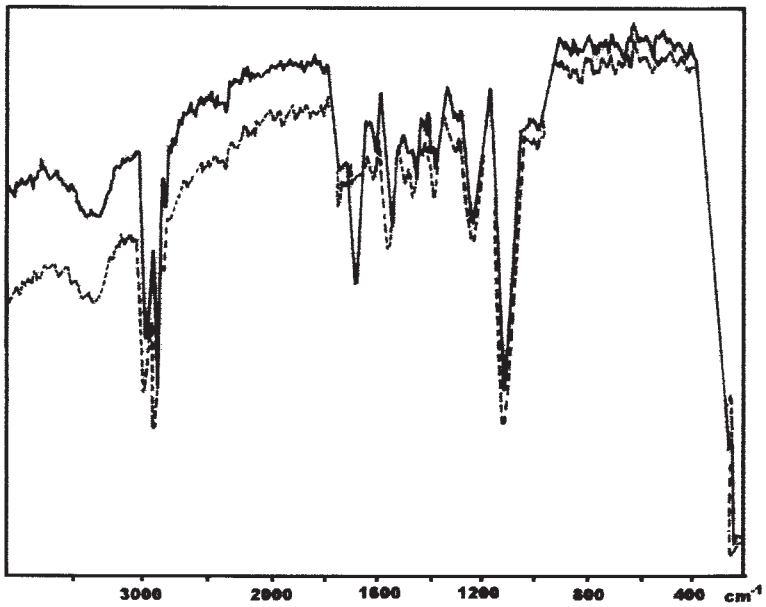


Figure 4 Changes in the IR absorption spectra of PU-1 film (—) before and (- - -) after UV irradiation for 6 h.

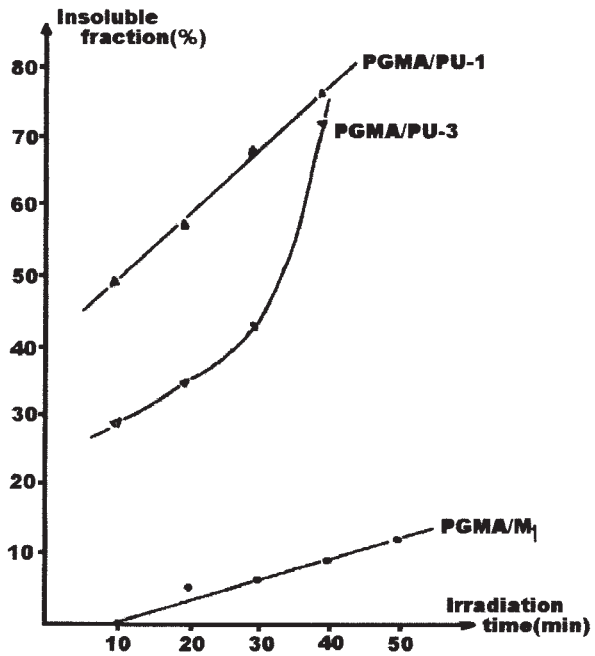


Figure 5 Variation of the insoluble fractions of PGMA/PU-1, PGMA/PU-3, and PGMA/M_1 films with the irradiation time.

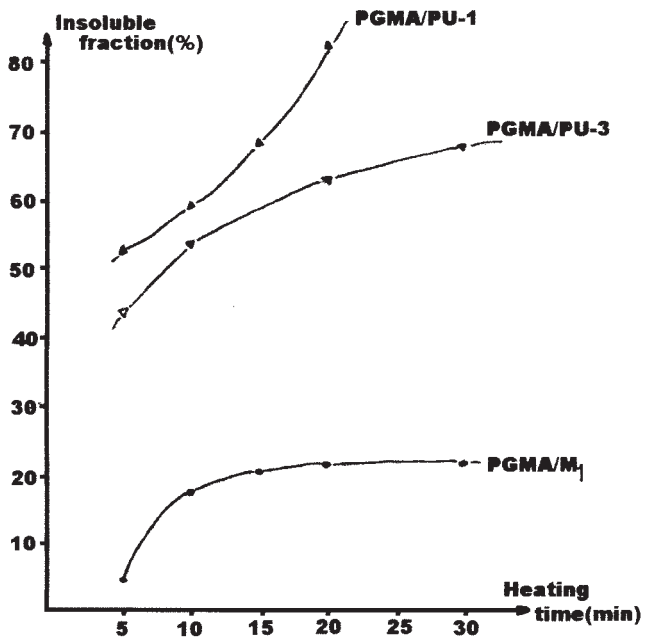
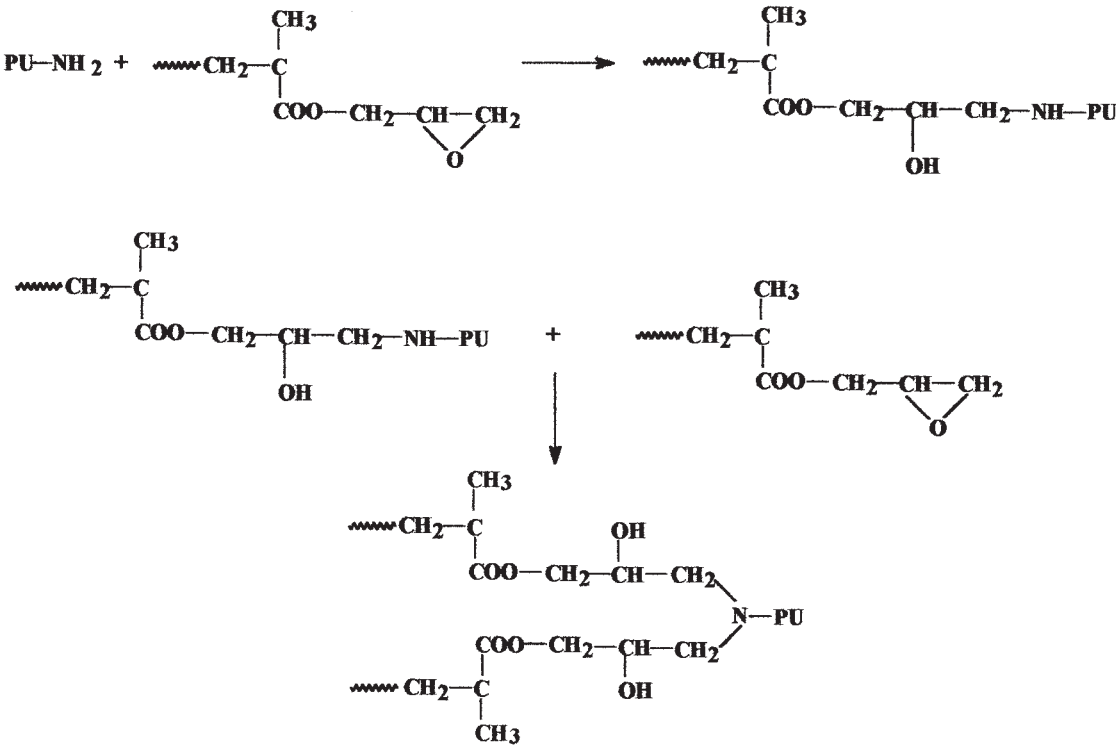


Figure 6 Effect of the heating temperature (100°C) and irradiation time (10 min) on the photocrosslinking of PGMA/PU-1, PGMA/PU-3, and PGMA/M_1 films.

In the same context, the insoluble fractions of PGMA films with 1 wt % PU-1 or 5 wt % PU-3 increased too with the irradiation time, reaching values over 70% (Fig. 5). A slight increase of only 12% in the film with 5 wt % monomer (after 50 min of irradiation) suggested that the monomer was much less efficient than the corresponding polymer in inducing the UV crosslinking of PGMA film. Such an effect could be



Scheme 3 Crosslinking of PGMA catalyzed by photogenerated amines.

correlated to the weight loss of aniline formed by radical stabilization through hydrogen abstraction, as well as its solubility in THF.

Under these circumstances (Fig. 6), the insoluble fraction in a PGMA/PU-1 film heated at 100°C and then irradiated for 10 min (82%) was higher than that of a PGMA/PU-3 film (63%). The results obtained through heating and irradiation–heating measurements for the same exposure time (20 min) showed that the amines photogenerated by the decomposition of oxime–urethane groups did indeed induce the thermal crosslinking of PGMA. The photogenerated amines opened the epoxy ring from PGMA and led to secondary amines, which reacted with other epoxy units to form crosslinks (Scheme 3).

Alternatively, a complementary test to determine the formation of aromatic amines consisted of a reaction with fluorescamine, a sensitive nonfluorescent reagent for the fluorometric determination of such groups.[18] In the first approach, a polymeric film (PU-1), irradiated for 30 min through a mask, was immersed in a 5 mM fluorescamine solution (4:1 v/v hexane/acetone), and a clear and blue fluorescent image was produced on the exposed zone. This observation suggested that a polyurethane with oxime–urethane units could find applications as a fluorescent image recording material, as reported by Choi and Chae[19] on poly(methyl acrylate)s with oxime–urethane units.[19] Further experiments on the photodecomposition of polymers of the same class and the photoinduced transformation of functional groups in polymeric chains are under investigation.

CONCLUSIONS

Three new polyurethanes with oxime–urethane groups incorporated with M were prepared, and their photobehavior as amine photobase generators was demonstrated. The photolysis of the aforementioned units led to the formation of amines, which induced the crosslinking of epoxy groups from PGMA upon heating, irradiation, and heating and irradiation. The photoprocess seemed to be favored by the combination of heating and irradiation, as illustrated by the higher values of the insoluble fractions of PGMA films with different contents of oxime–urethane moieties. Under suitable reaction conditions, a blue fluorescence was observed on an irradiated polymer film treated with fluorescamine.

References

1. Birbaum, J. L. U.S. Pat. 6,057,380 (2000).
2. Kutal, C.; Wilson, C. G. J Electrochem Soc 1987, 134, 2280.
3. Ito, K.; Shigeru, Y.; Kawata, Y.; Ito, M.; Tsunooka, M. Can J Chem 1995, 73, 1924.
4. Winkle, M. R.; Graziano, K. A. J Photopolym Sci Technol 1990, 3, 419.
5. Fréchet, J. M. J.; Matuszczak, S.; Lee, S. M.; Fahey, J. Polym Eng Sci 1992, 32, 1471.
6. Leung, M. K.; Fréchet, J. M. J.; Cameron, J. F.; Willson, C. G. Polym Mater Sci Eng 1993, 68, 30.
7. Mckean, D. R.; Wallraff, G. M.; Volkensen, W.; Hacker, N. P.; Sanchez, J. W.; Labadie, J. W. Polym Mater Sci Eng 1992, 66, 237.
8. Fréchet, J. M. J.; Cameron, J. F.; Chung, C. M.; Haque, S. A.; Wilson, C. G. Polym Bull 1993, 30, 369.
9. Mochizuki, A.; Teranishi, T.; Ueda, M. Macromolecules 1995, 28, 365.
10. Song, K. H.; Tsunooka, M.; Tanaka, M. J Photochem Photobiol A 1988, 44, 197.
11. Song, K. H.; Iwamoto, A.; Tsunooka, M.; Tanaka, M. J Appl Polym Sci 1990, 39, 1769.
12. Chae K. H. Macromol Rapid Commun 1998, 19, 1.
13. Chang, J. Y.; Kim, T. J.; Han, M. J.; Chae, K. H. Polymer 1999, 40, 4049.
14. Chae, K. H.; Song, H. B.; Ho, Y. S.; Chang, J. Y. Bull Korean Chem Soc 2000, 21, 7.
15. Chae, K. H.; Song, H. B. Polym Bull 1998, 40, 667.
16. Goddard, R. J.; Cooper, S. L. J Polym Sci Part B: Polym Phys 1994, 32, 1557.
17. Wicks, D. A.; Wicks, Z. W., Jr. Prog Org Coat 2001, 41, 1.
18. Gladilovich, D. B. Zh Anal Khim 1993, 48, 1507.
19. Choi, W. S.; Chae, K. H. Abstracts of the 6th International Symposium on Polymers for Advanced Technologies, Eliat, Israel, 2001; p 180.