

Synthesis and Properties of UV-Curable Poly(imideurethane) Acrylates

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ABSTRACT: Poly(imideurethane) acrylates (PIUAs) were obtained in solution by a three-step method, from cycloaliphatic diisocyanate, benzophenone tetracarboxylic acid dianhydride, three kinds of diols, and two kinds of monohydroxyacrylic esters (HEA, PETA). These polymers were used as components of the photosensitive compositions together with two reactive diluents and four photoinitiators. Using a mercury lamp (power 375 W) and Irgacure 907 as the photoinitiator some compositions spin coated on glass were cured rapidly within 10–30 s. In the preliminary photolithographic study with less advantageous exposure of

λ_{\max} 406 nm, patterns with 10- μm resolution were acquired. The cured PIUAs exhibited in thermogravimetric analysis a superior thermostability to 400°C than known poly(urethaneacrylates) and poly(urethaneimide) acrylates from aromatic diisocyanates. DSC and DMTA were used to characterize the thermomechanical stability and the glass-transition temperatures of the PIUA segments. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 971–980, 2004

Key words: poly(imideurethane) acrylates; photopolymerization; thermal properties; lithography; spin coating

INTRODUCTION

Photosensitive polymeric compositions are widely used for thin protecting or insulating layers, as adhesives, materials for microlithographic techniques in production of large-scale integrated circuits, and multichip modules for computers, to cite just a few applications.^{1–5}

Photosensitive compositions, containing polymeric precursors, photoinitiator or photoinitiating system, and active diluent, are applied by spin coating, screen printing, or spray coating. The photoinitiator used for the radical polymerization of vinyl groups should be characterized by a high absorption at a wavelength close to the λ_{\max} of the emission spectrum of the light source. The photoinitiator molecule should also have the high molar extinction coefficient of the incident light.⁶

For microelectronic applications the photosensitive precursors of aromatic polyimides are especially important because of the high thermal stability, high resolution of the patterns, low dielectric constant, high breakdown voltage and volume resistivity, and a low moisture uptake that may be achieved with these materials.^{1,3}

Between the working negative, photocrosslinkable polyimide precursors, the polyamic acid esters of un-

saturated alcohol or ammonium salts of polyamic acids with amines containing unsaturated, photosensitive groups are used.^{2,5}

In our previous work the synthesis and some properties of the photosensitive poly(urethaneimides) were described.⁷ These polymers were obtained from aromatic diisocyanates, oligoesterdiol or oligoetherdiol, dianhydride of the tetracarboxylic aromatic acid, and alcohol with acrylate, methacrylate, or allyloxy groups. The potential for use of such polymers for photocrosslinkable insulating layers and patterns was asserted. The thermostability of the finally formed poly(urethaneimides)⁸ was significantly superior compared to that of known polyurethane acrylates.⁹

In this work we describe the synthesis of new poly(imideurethane) acrylates (PIUAs) from benzophenonetetracarboxylic acid dianhydride (BTDA), 4,4'-methylenebis(cyclohexylisocyanate) (SMDI), and three kinds of diols and two kinds of monohydroxyacrylic esters. The cycloaliphatic diisocyanate with hydroxy compound used in the synthesis of PIUAs imparted to urethanes a characteristically higher thermal stability than could be obtained from the aromatic diisocyanates.¹⁰

The participation of urethane segments in PIUA offers the potential of obtaining layers with greater flexibility than that of those formed from typical polyimides. The obtained PIUAs were used as components of the compositions whose sensitivity to UV exposure and possibility for use in photolithography were investigated.

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EXPERIMENTAL

Materials and synthesis

In the synthesis of PIUAs we used the following materials:

- 4,4'-Methylenebis(cyclohexylisocyanate) (SMDI; Aldrich, Milwaukee, WI), a mixture of *cis-cis*, *cis-trans*, and *trans-trans* isomers, distilled under reduced pressure at 200°C.
- Benzophenone tetracarboxylic acid dianhydride (BTDA; Aldrich), recrystallized from acetic anhydride, washed with benzene, and dried under reduced pressure.
- Poly(butylene glutarate) diol (PBG; Aldrich), M_n 1000, dehydrated by heating at 90°C/h under reduced pressure (1.4 hPa).
- Bis(2-hydroxyethyl)phenyl ether (hydroquinone ethyl ether) (HQEE; Aldrich), dehydrated at 60°C/1.4 hPa for 3 h.
- 3-Alliloxyl-1,2-propanediol (glycerol- α allyl ether) (All-Gly; Gee Lawson Chemicals), dehydrated at 60°C/1.4 hPa/3 h.
- 2-Hydroxyethylacrylate (HEA; Aldrich), used in commercial form.
- Pentaerythritol triacrylate (PETA; Aldrich), used in commercial form.
- Solvent: dimethylformamide (DMF; POCh, Poland), dehydrated over P_2O_5 and distilled under reduced pressure.
- Catalyst: triethylene diamine (diazabicyclooctane) (DABCO; Houdry Hüls).

In the preparation of photosensitive compositions the photoinitiators, reactive diluents, and comonomer were used:

- 2-Methyl-1-[4-(methylthio) phenyl]-2-(4-morpholinyl)-1-propanone (Irgacure 907; Ciba Geigy, Summit, NJ).
- Dimethoxyphenylacetophenone (DMPA, Irgacure 651; Ciba Geigy), obtained from Aldrich.
- 4,4'-Dimethylaminebenzophenone [Michler's Ketone (MK), POCh, Poland].
- Isopropyltioxanton (ITX; Aldrich).
- *N*-Phenylmaleimide (NPM; Fluka Chemie, Buchs, Switzerland).
- 1,6-Hexanediol diacrylate (HDDA; Aldrich).
- Pentaerythrite tetraacrylate (TAPE; Aldrich).

Adhesion promoters used in processing:

- Silicone Rhodorsil primaire 10.057 CB.
- Hexamethyldisiloxane (HMDS).

Synthesis of poly(imideurethane) acrylates (PIUA)

PIUA was synthesized by a three-step method (Fig. 1). At first the imide precursor was obtained by the reac-

tion of SMDI and BTDA in DMF solution in the presence of 0.1 wt % of DABCO. The reaction at 90–95°C was carried out at a molar excess of SMDI until anhydride groups in the IR spectrum (1850 cm^{-1}) disappeared. In the next step the diol was added and the reaction was continued at the same temperature in an argon atmosphere. The advancement of the reaction was controlled by the decrease of OH group band ($3600\text{--}3400\text{ cm}^{-1}$) and the increase of the NH urethane band at 3370 cm^{-1} on IR spectra.

In the third step the alcohol containing the acrylate group was added with equimolar ratio of OH to free NCO groups and the reaction was continued at temperatures ranging from 70 to 90°C for more than 10 h in an argon atmosphere, until a stable level of NCO groups in the IR spectrum (2265 cm^{-1}) was reached.

In the synthesis of PIUA IV (Table I), after the reaction with PETA, HEA was added; this polymer contained an excess of OH groups.

The higher temperature of the reaction was not suitable because of the possibility of the adventitious reaction between diisocyanate and DMF,¹¹ and the possibility of thermal polymerization of the vinyl groups.

The intermediates and the PIUA samples were protected from light, oxygen, and water vapor. PIUA samples carrying the benzophenone group have photosensitivity and are intrinsically photoreactive⁵; in the processing step, oxygen absorbed from the air may reduce the photopolymerization rate because O_2 reacts as a scavenger of initiating radicals.⁶ Protection from water makes impossible the reaction of free NCO groups with H_2O and change of the PIUA solution viscosity.

Figure 1 shows the scheme of the synthesis and the components and designation of the obtained PIUAs are listed in Table I.

Preparation of the photosensitive compositions

To 76.5 parts of the obtained solutions (25 wt %) of PIUAs I–VII (Table I), 20 parts of the reactive diluent and 3.5 parts of the photoinitiator (Irgacure 907) were added (Table II). Before the investigation of photosensitivity the compositions were protected from light.

From the PIUA IV sample the compositions with other photoinitiators and with NPM as the comonomer were also prepared (Table III).

Characterization methods

Process of pattern formation

Preliminary investigation. Solutions of the photosensitive compositions containing PIUA were coated onto glass plates ($30 \times 60\text{ mm}$), previously covered by silicone as a promoter of adhesion. The spin coating

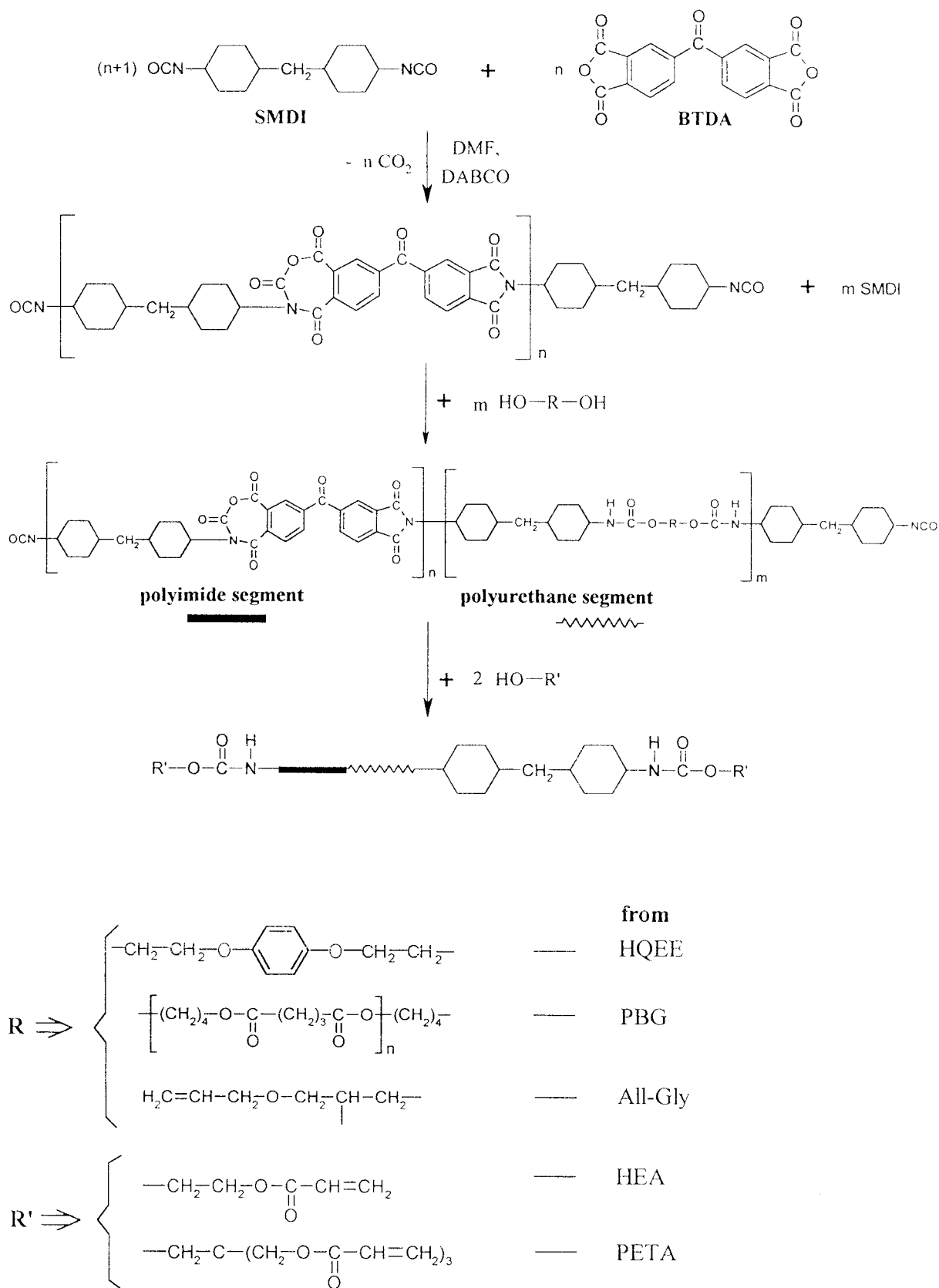


Figure 1 Scheme of the PIUA synthesis.

TABLE I
Components in PIUA Synthesis

PIUA	Components	Molar ratio	Polyimide segments content, ^a (mass %)
I	SMDI : BTDA : HQEE : HEA	2.5 : 1 : 1 : 1	41.2
II	SMDI : BTDA : HQEE : PETA	2.5 : 1 : 1 : 1	35.8
III	SMDI : BTDA : HQEE : PETA	2.5 : 0.5 : 1.5 : 1	27.7
IV	SMDI : BTDA : HQEE : PETA : HEA	2.5 : 1 : 1 : 1 : 2.12	30.4
V	SMDI : BTDA : HQEE : PBG : PETA	2.5 : 1 : 0.67 : 0.33 : 1	30.1
VI	SMDI : BTDA : HQEE : All-Gly : PETA	2.5 : 1 : 0.67 : 0.33 : 1	35.2
VII	SMDI : BTDA : HQEE : PBG : All-Gly : PETA	2.5 : 1 : 0.25 : 0.25 : 0.5 : 1	31.9

^a Calculated as the ratio of the weight of BTDA and weight of the equimolar quantity of SMDI to the total weight of the reagents; the evolution of CO₂ was taken into account.

was run for 10 s at 700 rpm with use of the prototype laboratory centrifuge. After evaporation of the solvent at vacuum (50°C/30 min/1.4 hPa), the sample was exposed (in air atmosphere) to UV irradiation using a mercury lamp (Famed L6/58, Poland, power 375 W), in a distance of 12 cm, by use of a provisional mask constructed from black paper. Development of the pattern was carried out by immersion in a mixture of DMF and toluene (4:1 vol). The sample was then dried and heated at 150°C/3 h under reduced pressure (1.4 hPa) for full imidization.

Photolithographic study. Photosensitive PIUA compositions were spin-coated onto a GaAs substrate (10 × 10 mm), previously covered by HMDS. After vacuum drying at 50°C/40 min, the curing was accomplished with a Carl Süß MA 56 apparatus, under mercury lamp (irradiation power 18 mW/cm²) at 406 nm, with a vacuum Cr contact mask. The development, drying, and final heat treatment were carried out as described in the preceding section.

Infrared and UV spectroscopy

IR spectroscopy was performed with use of the Specord IR (Carl Zeiss, Jena, Germany) or Bruker IFS66 spectrometer (Bruker Instruments, Billerica, MA). The prepolymer films on NaCl were analyzed after evapora-

tion of the solvent (50°C/30 min/1.4 hPa). The IR spectra were also obtained for the polymer films on NaCl after photocuring and after thermal imidization.

UV absorbance spectra were recorded with a UV/VIS Lambda 18 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

Thermogravimetric analysis (TGA)

TGA was accomplished with an OD 102 derivatograph (MOM, Hungary) at a heating rate of 6°C/min and the sensitivity of TGA, 200.

Differential scanning calorimetry (DSC)

DSC was performed with the Perkin-Elmer DSC 7 apparatus, at a heating rate of 20°C/min.

Dynamic mechanical thermal analysis (DMTA)

DMTA was carried out with bending on a Polymer Laboratories DMTA Mk III analyzer (Poole, UK) at a heating rate of 4°C/min and a frequency of 1 Hz.

RESULTS AND DISCUSSION

The 25 wt % PIUA solutions obtained from the reagents listed in Table I were used as components of the photo-

TABLE II
Photosensitive Compositions from PIUAs (76.5 wt %), Irgacure 907 (3.5 wt %), and HDDA or TAPE (20 wt %)

Photosensitive composition	PIUA ^a	Reactive diluent	Concentration of vinyl πc_{π} (mmol/g)		Curing time (Famed lamp) (s)
			In PIUA	In compositions	
A	I	HDDA	0.77	4.59	300
B	II	HDDA	2.03	5.00	180
C	III	TAPE	2.12	6.26	30
D	II	TAPE	2.03	6.16	30
E	V	TAPE	1.73	5.79	20
F	VI	TAPE	2.45	6.33	20
G	VII	TAPE	2.13	6.06	10

^a According to Table I.

TABLE III
Photosensitive Compositions from PIUA IV ($C\pi = 2.96$) and Other Additives^a

Composition	Comonomer	Photoinitiating system	Reactive diluent	Concentration of vinyl πc_π (mmol/g)	Curing time (Famed lamp) (s)
H	—	Irgacure 907 (3.5)	HDDA (20)	5.30	300
K	NPM (7.4)	Irgacure 651 (0.2), MK (0.4)	HDDA (18.4)	4.73	780
L	NPM (7.4)	Irgacure 907 (0.2), MK (0.4)	HDDA (18.4)	4.73	660
M	—	Irgacure 907 + ITX (1:1 mol) (3.5)	HDDA (20)	5.30	360

^a Weight percentage ratios are in parentheses.

sensitive compositions listed in Tables II and III. After photocuring and heating at 150°C/1.4 hPa the hard, light yellow, and transparent polymer films were obtained.

The low viscosity of the PIUA solutions, obtained in the described parameters of the synthesis (to 16 mPa s⁻¹) allows them to be coated by a spraying machine.

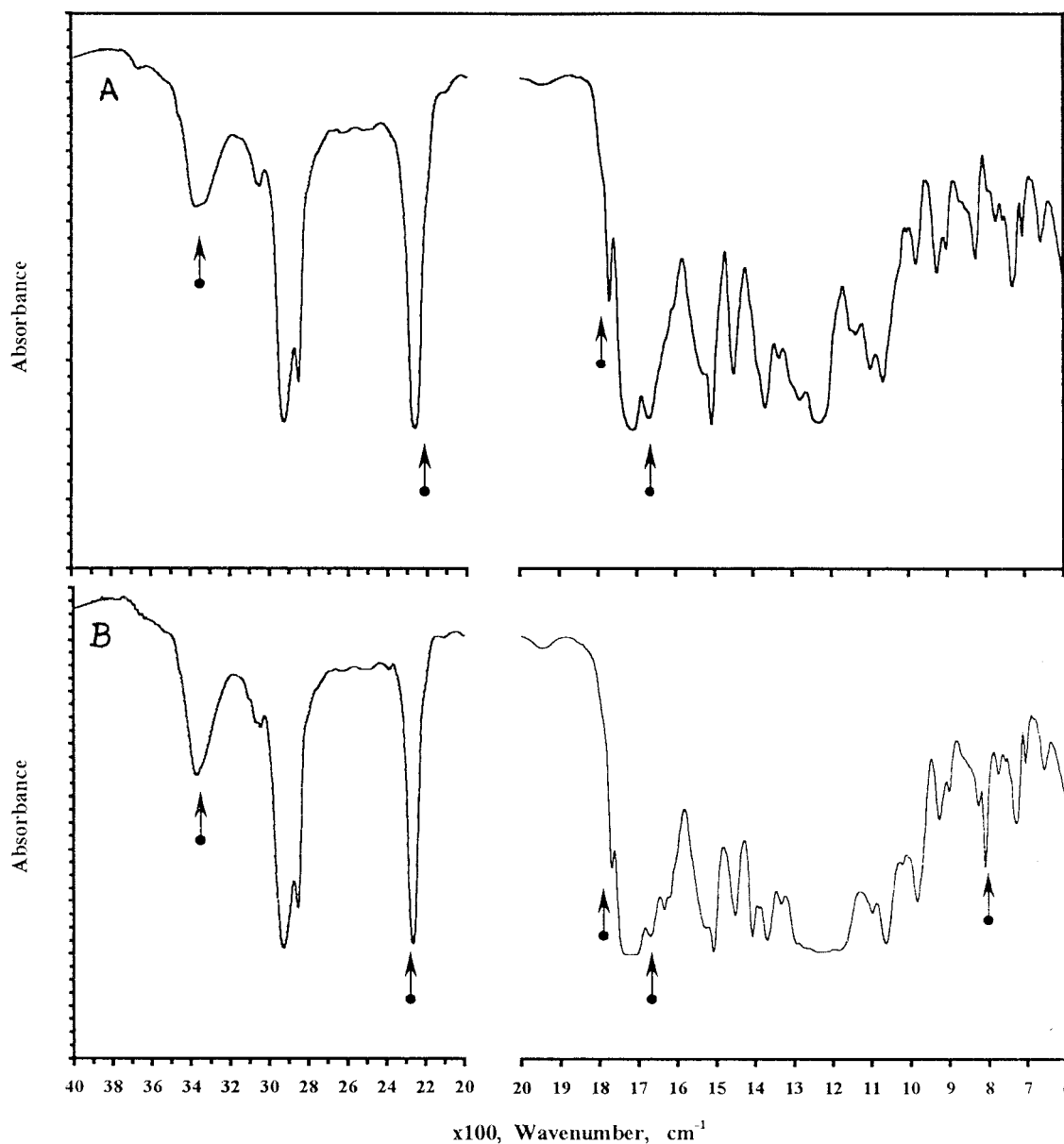


Figure 2 Infrared spectra (Bruker): (A) poly(imideurethane) (PIU) from SMDI, BTDA, and HQEE; (B) PIUA II from PIU and PETA. Characteristic bands in text.

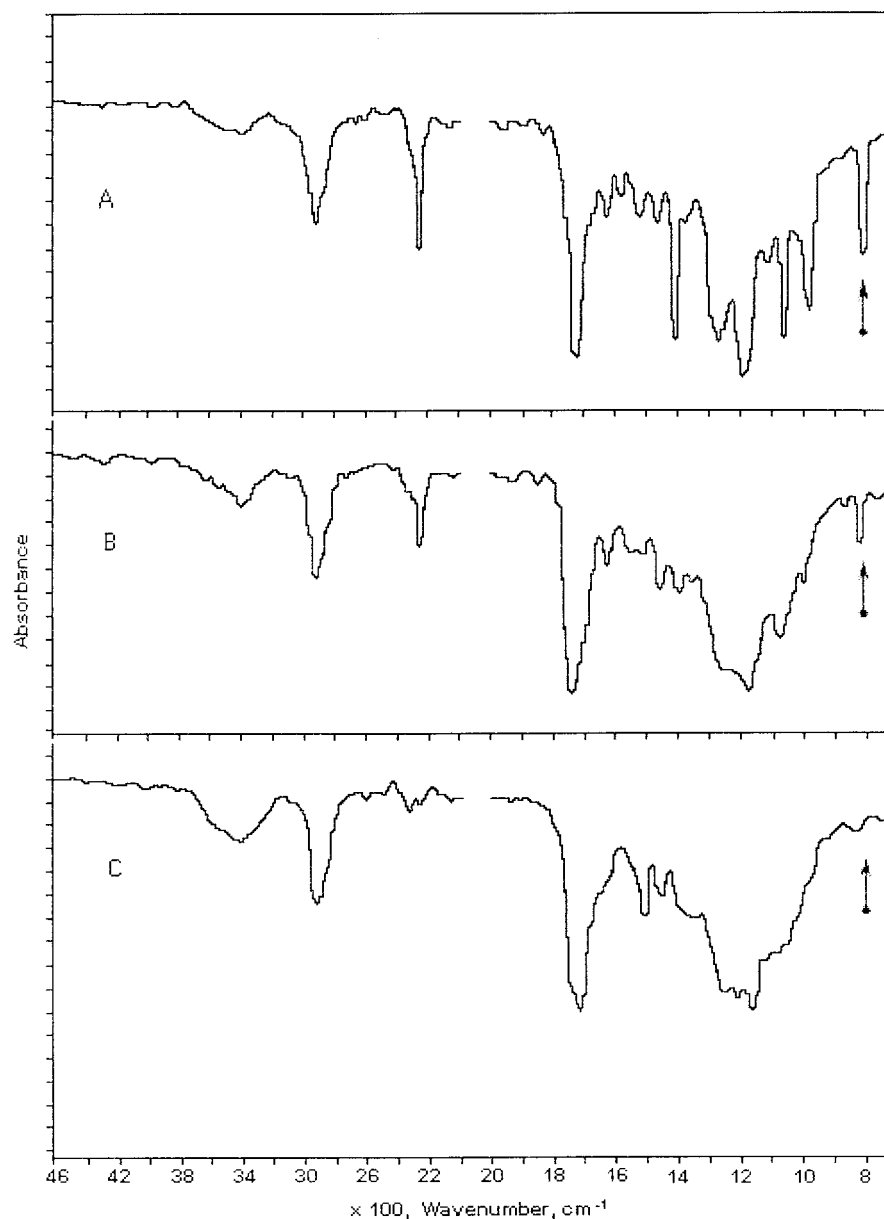


Figure 3 Infrared spectra (Specord IR) of the F composition from PIUA VI and TAPE: (A) after evaporation of the solvent (30 min/1.4 hPa/50°C); (B) after photocuring at 10 s with the Famed mercury lamp; (C) after heat treatment at 150°C/1.4 hPa/3 h.

Investigation of PIUA by infrared spectroscopy

Figure 2(A) presents the IR spectrum for the polyimideurethane (PIU) obtained from the reaction of oligoimide (BTDA-SMDI) with HQEE. The absence of the anhydride C=O band at 1850 cm^{-1} confirmed that BTDA reacted with SMDI. Figure 2(B) shows the product of the reaction of PIU with PETA (PIUA II).

In the fixed conditions of the synthesis the equilibrium of the NCO and OH groups was observed, which was unchanged after a prolonged time at temperatures ranging from 70 to 90°C. On the IR spectra the presence of the OH groups at 3600–3400 cm^{-1} was observed as a small shoulder of the N—H band (3370

cm^{-1}), which disappeared, with the NCO band at 2260 cm^{-1} after heating at 150°C. At this temperature, under reduced pressure (1.4 hPa) the final decarboxylation of the seven-membered ring (imidization) and further polymerization and curing were achieved.

The photocuring of the PIUA under UV exposure and past heat treatment was observed in IR spectra by diminishing the $-\text{CH}=\text{CH}_2$ band at 810 cm^{-1} (Fig. 3).

Dependency of the photocuring time on the PIUA composition and exposure parameters

The curing time under UV exposure was dependent on the structure of PIUA, particularly on the concen-

tration of vinyl groups (c_{π}) in the polymer and in the photosensitive composition. The indispensable photocuring time was also dependent on the type of mercury lamp, its λ_{\max} and power, and on the photoinitiator or photoinitiating system. Tables II and III present the preliminary investigation of PIUA photocuring on glass plates with the Silicone Rhodorsil used as the adhesion promoter.

As shown, the use of PETA instead of HEA in the synthesis of PIUA and the use of TAPE instead of HDDA as a reactive diluent led to a greater c_{π} in the photosensitive composition and to shortening the exposure time, necessary for obtaining the polymer layers or durable patterns at the development stage (see compositions A–C, Table II). Composition G from PIUA VII, of higher molecular weight, connected with use of PBG in the synthesis, required the shortest time for curing (Table II).

Because of the presence of the benzophenone structure in PIUA with λ_{\max} at 260 nm^{6,12} we primarily used Irgacure 907 as a photoinitiator, with λ_{\max} at 306 nm⁶ (Fig. 4). The difference between the wavelength of the maximum absorption for the photoinitiator and monomer or polymer precursor is advantageous for initiating the polymerization and curing process, by the radicals originating from the photoinitiator.¹³

For composition K containing Irgacure 651 (DMPA) with λ_{\max} at 250 nm⁶ the longer exposure time was necessary for full curing of PIUA (Table III).

From Table III one may observe that the considerable decrease of the Irgacure 907 content in composition L led to the increase of the curing time, despite the additional presence of the other photoinitiator (the Michler's Keton) and NPM as a comonomer of the polymerization. Michler's Keton is often cited in research works,⁶ although now it is not recommended for use because it is a carcinogenic compound.

The ITX photoinitiator of high extinction coefficient

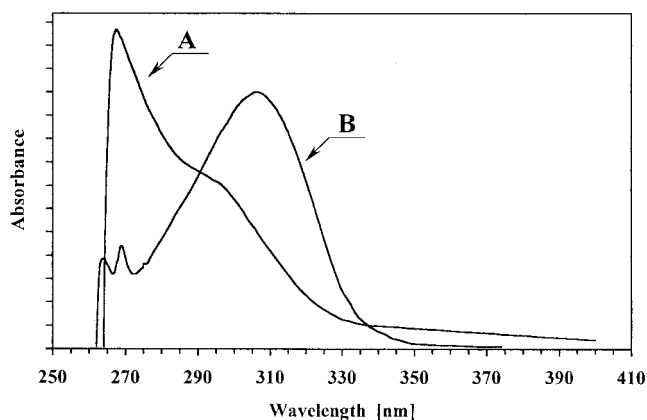


Figure 4 UV spectra of the PIUA VII + TAPE (A) and Irgacure 907 (B).

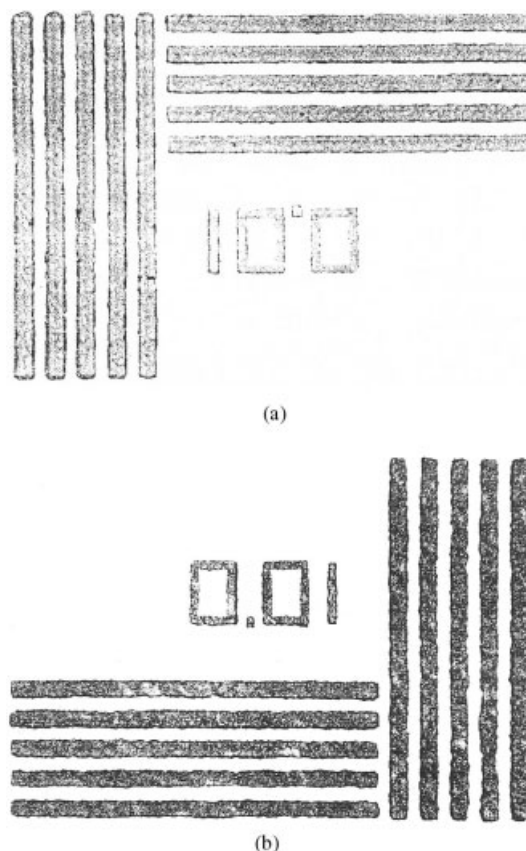


Figure 5 Microscopic photography ($\times 300$) of the photolithographic patterns from the F composition at 60-s exposure time (A) and from the C composition at 30-s exposure time (B).

at 360 nm⁶ has a curing activity close to that of Irgacure 907 (Table III).

The preliminary photolithographic study on the GaAs substrate, using the mercury lamp of exposure power of 18 mW/cm² at 406 nm confirmed that from the investigated PIUA compositions C, D, E, and F (Table II), at an exposure time of 30–60 s, it is possible to obtain patterns with a resolution of 10 μm (thickness 2 μm) [Fig. 5(A), (B)].

It seems that by using the mercury lamp of emission λ_{\max} close to the λ_{\max} of the used photoinitiator in PIUA compositions it would be possible to achieve a better resolution of the patterns and a shorter curing time in the photolithographic investigations. The change of the adhesion promoter, for example, using γ -aminopropyl triethoxysilane^{14,15} instead of HMDS, will probably lead to better durability of the patterns at the developing stage.

Thermal stability of the UV-cured PIUAs

Investigation by TGA of the polymers obtained from the PIUA compositions, after their photocuring and thermal imidization, shows the dependency of their

TABLE IV
Thermogravimetric Analysis of the Cured PIUAs^a

Composition polymer ^b	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Mass retention (%)	
				At 400°C	At 500°C
A	280	332	430	70	25
C	310	340	435	77	25
D	330	370	435	82	25
E	317	347	450	77	27
F	302	345	442	78	29
G	304	350	445	79	22
H	256	320	422	62	30

^a T_5 , T_{10} , temperatures of 5% and 10% weight loss, respectively; T_{max} , temperature of the maximal weight loss rate.

^b According to Tables II and III.

chemical thermostability on the PIUA structure, particularly on the polyimide segment content and crosslinking density (Table IV).

The polymers emanating from the A and H compositions, based on PIUAs terminated completely or partially by HEA (PIUAs I, IV, Table I) and cured in the presence of HDDA are characterized by lower temperatures of thermal decompositions (T_5 , T_{10} , T_{max}) compared to that of other PIUAs terminated by PETA and crosslinked with TAPE (Table IV).

PIUA IV, the main component of the H composition, was obtained with the excess of OH groups from HEA, which explains the lowest thermostability of the polymer obtained from this composition (Table IV).

The polymer from composition D, obtained from PIUA II, characterized by the highest polyimide content and high crosslinking, has the best thermostability (Table IV). High T_5 , T_{10} , and T_{max} temperatures were also observed for the polymer from composition E, based on PIUA V, containing comparatively longer urethane segments obtained with PBG participation. Polymers formed from the F and G compositions based on PIUAs VI and VII, obtained with a share of All-Gly show lower initial decomposition temperatures (T_5 , Table IV), which may be attributed to the lower density of these polymers.

Most of the cured PIUAs retained up to 70 mass % at 400°C; the temperature of the maximal rate of decomposition was in the range of 420–450°C (Table IV). From these TGA data it is seen that UV-crosslinkable PIUAs have much better resistance to thermal decomposition than UV-cured polyurethane acrylates for which T_{max} at 330–370°C and mass retention at 400°C of 48–63% were measured.⁹

Except for the polymers from compositions A and H, other UV-cured PIUAs from this study are more resistant to thermal decomposition to 400°C than the cured photosensitive poly(urethaneimides) from aromatic diisocyanates, which we described previously.⁸

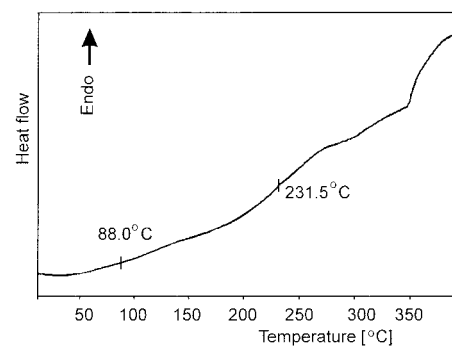
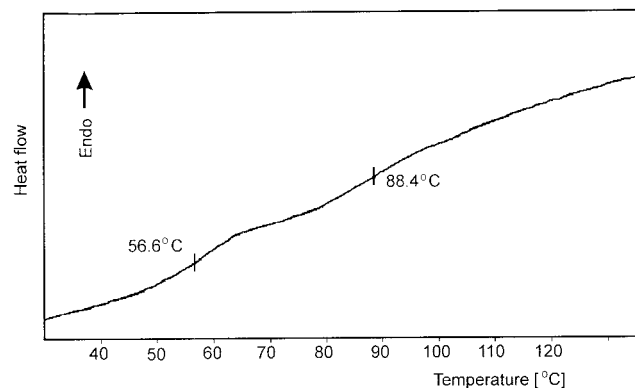


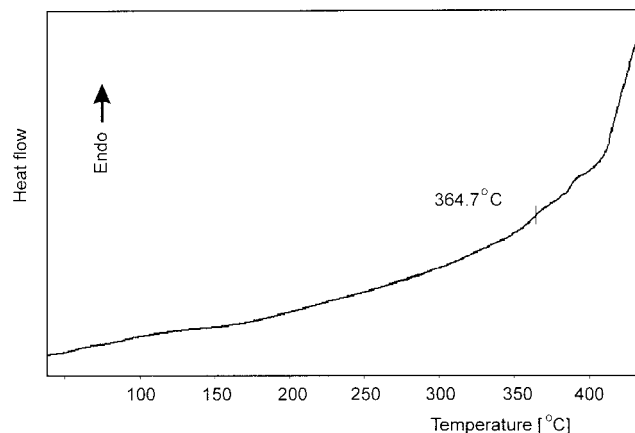
Figure 6 DSC thermogram of the crosslinkable polymer from D composition of PIUA II.

DSC analysis of the UV-cured PIUA from composition D, based on PIUA II and TAPE, shows the glass-transition temperature (T_g) of the urethane segments at 88°C and the T_g of the polyimide segments at 231°C (Fig. 6).

Figure 7(A) exhibits the DSC curves of the polymer from composition E based on PIUA V obtained with



(a)



(b)

Figure 7 (A) and (B) DSC thermograms of the crosslinkable polymer from E composition of PIUA V.

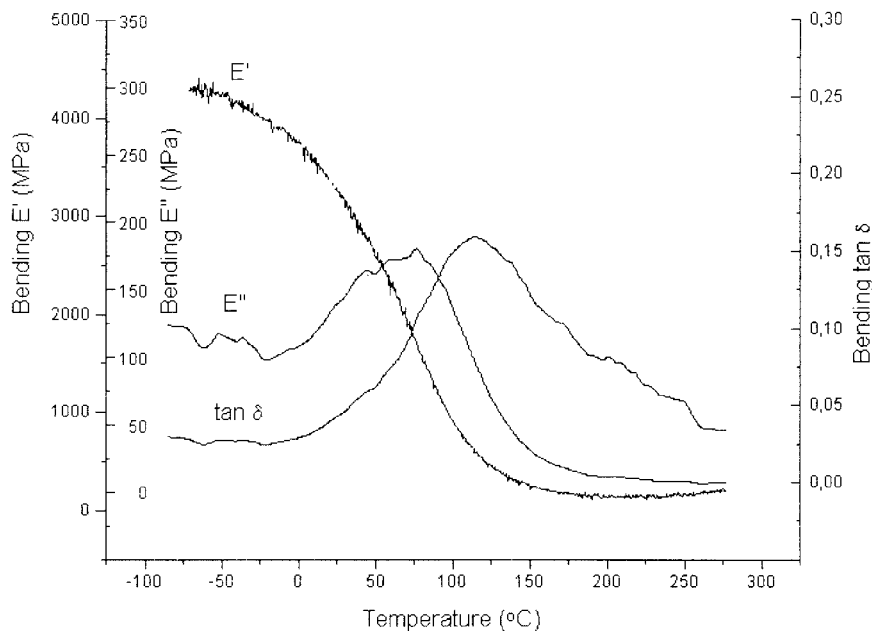


Figure 8 Thermal dependency of the dynamic mechanical moduli E' (storage) and E'' (loss) and the loss factor $\tan \delta = E''/E'$ for the crosslinkable PIUA V from the E composition.

participation of the oligoesterdiol (PBG) beside the same reagents as used in the synthesis of PIUA II. For this polymer two T_g values of the urethane segments are observed: at 57°C, for the urethane segments from PBG, and at 88°C, for the urethane segments from HQEE. The T_g of the polyimide segments in this cured polymer was designated at 364°C [Fig. 7(B)].

Such a significant difference between the T_g values of the polyimide segments of the PIUA from compositions D and E is probably attributed to the much stronger interaction of these segments with the urethane segments of a great density of polar urethane groups in PIUA II.

The DSC analysis was performed at a heating rate up to three times greater than the TGA and this is the reason that the designated T_g of the polyimide segments in the polymer from composition E is close to the decomposition temperature from TGA (Table IV).

At the temperature range from -100 to 280°C, the thermomechanical stability investigated by DMTA at the bending mode is shown in Figure 8 for the cured PIUA-E composition. From the wide maximum of the loss modulus (E'') the T_g of the urethane segments is observed at 70–90°C. The connected peak of $\tan \delta = E''/E'$ is designated at 113°C.

The storage modulus of elasticity (E'), which was high at room temperature (3260 MPa), decreases with temperature, but even at 150°C the E' value is considerable (236 MPa) (Fig. 8, results E'). For the polyurethane acrylates and polyurea acrylates, by DMTA at the tension mode, a greatly diminished thermostability of E' was described.¹⁶

CONCLUSIONS

PIUAs obtained in this work from cycloaliphatic diisocyanate can be used as photosensitive materials characterized by good thermostability. In compositions with pentaerythrite tetraacrylate and Irgacure 907, using a mercury lamp at 375-W power, PIUAs were cured rapidly within 10–30 s, giving hard layers and patterns. In the photolithographic study with the lamp at an exposure power of 18 mW/cm² at 406 nm for 30–60 s, patterns with a resolution of 10 μ m were acquired.

The aim of further study will be synthesis of PIUAs of greater solution viscosity, the choice of an optimally suitable adhesion promoter, and better parameters for the spin coating.

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