Novel UV-Autocurable Methacrylo-Urethane Polymeric Films Derived from *m*-Digallic Acid: Preparation and Characterization

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ABSTRACT: A new acrylo-urethane film polymer was obtained from methacrylic *m*digallic acid derivatives. The product was attained either by thermo- or photopolymerization, and the films were characterized by chemical and spectroscopic methods. Other studies of the properties of these polymers were also performed. The main characteristics found were brief curing times achieved with no photoinitiators, good thermal properties, and optical activity. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2575–2583, 1998

Key words: polymer synthesis; photocrosslinking; urethanes; *m*-digallic acid

INTRODUCTION

During the last 20 years an ever growing number of resins that are readily polymerizable under UV radiation, in particular the very reactive multifunctional acrylates and methacrylates, were commercialized when the many advantages of this new technology became apparent.^{1–3}

In general, photocurable resins primarily consist of monomers or oligomers with acrylic or methacrylic double bonds. For fast and efficient curing of such resins it is necessary to include more than one terminal double bond, because monofunctional acrylates lead to a decreased modulus and increased ductility, whereas multifunctional acrylates lead to the opposite. In addition, multifunctional diluents show a higher response to radiation.^{4–8}

The reactive oligomer is the most important component in determining mechanical properties of a radiation curable coating system. Acrylated urethanes as a class combine the well-known specific properties of conventional urethane coatings (higher abrasion resistance, toughness, tear strength, and good low-temperature properties) with the superior optical properties and weatherability of polyacrylates.^{9–12}

The aim of this research work was the synthesis and characterization of a novel, easily prepared multifunctional acrylo-urethane polymer that could undergo rapid photoinduced radical polymerization.

This material was prepared in high yields using simple, readily available starting materials such as *m*-digallic acid (*m*-DA, also known as tannic acid by many authors), 2-hydroxyethyl methacrylate (HEMA), and toluene 2,4-diisocyanate (TDI). Besides, the introduction of additional aromatic groups as stiffening agents into monomer units often improves the mechanical characteristics and bestows a toughening effect to the resulting polymer. According to this, a polymer containing multiacrylic urethane functional groups combined with an *m*-DA methacrylic derivative was achieved.

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Figure 1 Reaction scheme of the synthesis of the functionalized precursors: **I**, *m*-DA; **II**, toluene 2,4-diisocyanate (TDI); **III**, intermediate monomer; **IV**, 2-hydroxyethyl methacrylate (HEMA); **V**, functionalized precursor.

EXPERIMENTAL

Reagents and Materials

The *m*-DA (MW 323) was purchased from Mallinckrodt as tannic acid and was dried in a vacuum at 60°C for 3 days before use. TDI (Petroquímica Río Tercero) was used without any further purification, and its —NCO number¹³ was found to be 47.9% (w/w) (purity, 99.1%). HEMA (Fluka), stannous octoate (Petroquímica Río Tercero), benzoyl peroxide (BPO), and hydroquinone were used without any further purification. The HEMA methacrylic group number¹⁴ was 0.988 eq/mol.

Tetrahydrofuran (THF; Riedel-de Häen) was refluxed over KOH for 4 h and later distilled and dried under molecular sieves; *n*-butanol (*n*-BuOH) (Sintorgan) was reagent grade.

Synthesis of Methacrylo-Urethane *m*-DA Based Polymer

A one-step synthetic pattern was assayed in order to obtain the photocurable precursors (V) from

m-DA. An idealized scheme of synthesis is shown in Figure 1.

Procedure

The amounts of 10.5 g (60 mmol) of TDI and 200 mL of THF were introduced into a three-necked flask equipped with a nitrogen inlet, dropping funnel, magnetic stirrer, and a condenser with $CaCl_2$. The solution was stirred in a water bath, and 6.5 g (20 mmol) of *m*-DA dissolved in 30 mL of THF was added dropwise (molar ratio *m*-DA : TDI = 1 : 3) for 30 min. Once the addition was completed the reaction temperature was raised to 30°C and the mixture was stirred for 95 min. A yellowish, viscous solution was obtained.

In the second stage of the reaction, 0.1% (w/w) stannous octoate and 100 ppm hydroquinone were added into the mixture, and 7.8 g (60 mmol) of HEMA dissolved in 20 mL of THF were added dropwise for 30 min. After completion the reaction temperature was raised to 45°C and the mixture was stirred for 170 min. Once the reaction was finished the solvent was evaporated in a vac-

uum and a stoichiometric amount of n-BuOH was added to cap the unreacted NCO groups.¹⁵

The obtained solution was dried and used in the polymerization studies without any further purification.

Polymerization Reactions

Two different curing methods were applied in obtaining the polymers: thermal and photochemical.

Thermal Curing

Two milliliters of the 15% (w/v) solution in *n*-BuOH obtained above containing 1% (w/w) of BPO as initiator were poured into Petri dishes (58 \times 15 mm) and then evaporated in a vacuum system. The dishes were placed in an oven, and the temperature was raised to 80°C for 75 min. The obtained resin was named polymer I-T, and it was purified by fractional precipitation: 100 mg of cured resin were dissolved in 5 mL of MeOH, and then 15 mL of chloroform (nonsolvent) were added using a magnetic stirrer. The precipitate was separated by centrifugation, exhaustively washed with chloroform, and dried in a vacuum at room temperature for 24 h.

Photochemical Curing

No photoinitiator was used in this method. The sample preparation procedure was the same as above, and the dishes were irradiated by a 125-W medium-pressure mercury lamp (Engelhard–H-anovia) for 20 min. This new resin was called polymer I-P, and it was purified by washing with acetone in a Soxhlet extractor: 100 mg of cured resin were placed in the extractor using 300 mL of acetone, and the process was run for 24 h.

Characterization

IR spectra performed on polymers I-T and I-P were taken with a Nicolet 5-SXC FTIR spectrophotometer. Solid samples were mixed with a few miligrams of KBr to form disks. The Fourier selfdeconvolution technique¹⁶ was also used to study the number of individual peaks that were overlaid by the carbonylic broader band.

The ¹H-NMR spectrum of polymer I-T was obtained on a Bruker AC 200 spectrometer using deuterated DMF and tetramethyl silane, as the internal standard. The chemical shift was given in parts per million (ppm). The optical activity of polymer I-T was measured with a Jasco DIP 370 polarimeter at CEPROCOR Labs, using the sodium D-line wavelength (589 nm) and a 1.22% (w/v) solution in acetone. Specific rotation [α] was determined by

$$[\alpha]_{\lambda}^{t} = 100 \alpha/bC$$

where λ is the current wavelength, *t* is the temperature (20°C), α is the observed rotation, *b* is the path length in decimeters, and *C* is the concentration in grams per 100 mL of solution.

TGA studies (polymer I-P) were made on a Netzsch STA 429 thermogravimetric analyzer at CIMM Labs. The system was purged with nitrogen and heated at a rate of 10°C/min from room temperature to 900°C. Both TGA and its derivative (DTG) were plotted simultaneously versus temperature.

The gel content was determined on photocured films at different time lengths. The films were washed with acetone, and the residual polymers were dried in a vacuum.

The determination of the swelling index (SI) and swelling percentage (SP) of polymer I-P was made by means of a modified technique of the ASTM standard D 3616-77. The values were calculated from

$$SI = V_S/V_D$$

where $V_{\rm S}$ and $V_{\rm D}$ are the volumes of the swollen gel and dried gel, respectively, and

$$SP = 100[(W_{S} - W_{D}]/W_{D}]$$

where $W_{\rm S}$ and $W_{\rm D}$ are the weights of the swollen gel and dried gel, respectively.

RESULTS AND DISCUSSION

Synthesis and Photocrosslinking

Figure 1 depicts the synthetic scheme of polymer I, in which an idealized structure is represented for products III and V. Such products were synthetized from a coupling reaction between *m*-DA and TDI (intermediate III) followed by HEMA addition to form precursor V using a ratio of TA : TDI : HEMA of 1 : 3 : 3. Lower ratios than the one used (1 : 1 : 1) led to a mixture of products with an average number of methacrylic equivalents of 1.5. On the other hand, higher ratios of

TA : TDI : HEMA (1:3:10) led to products with the same relationship of monomers found for the TA : TDI : HEMA ratio of 1 : 3 : 3.

It should be stated that several isomeric products can be obtained in the first stage of the reaction (intermediate **III**) according to the relative reactivity of phenolic hydroxy groups from *m*-DA. Therefore, the precursor V can contain a mixture of isomers according to the relative reactivity of the —NCO groups¹¹ ($k_{\text{ortho}} = 25$; $k_{\text{para}} = 262$ at 25°C). However, FTIR and ¹H-NMR characterization studies, which will be further discussed, allowed us to show that the precursor V carries the most feasible structure and monomer ratio. This synthetic procedure offered an efficient method for preparing the precursor products with yields of 70-75%.

Polymerization process was directly applied on precursor **V**, which was not previously purified.

Polymer I was obtained either by thermal or photocrosslinking of the methacrylo-urethane m-DA functionalized precursor products (V).

Characterization

Table I shows the curing parameters and general properties found on the resins. It may be inferred from this data that cured films turned into hard, bright, and transparent products of dark yellow color (polymer I-T) and light yellow color (polymer I-P).

Thermal curing applied on the functionalized precursor led to a product (polymer I-T) that was soluble in methanol, acetone, THF, and DMF. Photochemically cured films (polymer I-P) showed an appreciable crosslinking degree, because the obtained products were completely insoluble in such solvents.

Characterization studies were performed on purified samples of polymer I-T obtained by fractional precipitation (using MeOH as the solvent and chloroform as the nonsolvent) and polymer I-P obtained from Soxhlet extraction.

IR Spectroscopy

The IR spectrum performed on polymer I-T showed the same pattern as that plotted for polymer I-P. The main bands were ν_{O-H} phenolic and ν_{N-H} ure thane (3500–3100 cm⁻¹); $\nu_{C=O}$ acid, ester, and urethane (1780–1685 cm⁻¹); $\nu_{C=CH_2}$ residual vinyl groups (945 cm⁻¹); $\sigma_{\rm C-H}$ out of plane deformation and 1,2,3,5-aromatic ring substitution (883 and 774 cm⁻¹); $\sigma_{\rm C-H}$ out of plane defor-

	Purification Method	Fractional precipitation solvent: acetone nonsolvent: chloroform Washing by Soxhlet	5
Properties of Polymerized Films	Insolubility	Benzene, chloroform, toluene, dioxane Acetone, MeOH, THF, DMF,	chloroform
	Solubility	MeOH, acetone, THF, DMF –	
	Color	Dark yellow Light yellow	
	Appearance	Hard, transparent and bright	
	Curing Temp. (°C)	80 25	
	Curing Time (min)	75 20	
	Initiator	BPO	
ers and General	Curing Method	Thermal Photochemical	
ring Paramete	Stabilizer	Hidroquinone (100 ppm)	
Fable I Cu	NCO Capping Agent	3 n-BUOH	
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methacrylic functionality; BPO, benzoyl peroxide

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Figure 2 FTIR spectrum of polymer I-P.

mation and 1,2,4-aromatic ring substitution (822 cm^{-1}). Figure 2 shows the spectrum obtained from polymer I-P.

The deconvoluted zone of the carbonyl groups of this polymer (Fig. 3) clearly shows three peaks at 1776, 1737, and 1689 cm⁻¹, the latter two corresponding to ester and urethane groups, respectively. The band at 1776 cm⁻¹ is a typical band of nonassociated acid groups. Their appearance in the spectrum may be attributed to the lack of mobility shown by the macromolecule. Therefore, the steric hindrance plays an important role in the acid groups association, causing a gradual shift of the C=O absorbance toward higher frequencies as molecular weight increases.

A detailed analysis of the deconvoluted zone of the carbonyl groups was made by considering a ratio between the relative absorbances due to ester groups (1737 cm⁻¹) and urethane groups (1689 cm⁻¹). The calculations of the relative values of the molar extinction coefficients (ε) for C=O urethanes and C=O esters were established by means of a reference sample from the reaction between *p*-tolyl isocyanate and HEMA in a ratio of 1 : 1. Consequently, if [C=O] represents the relative concentrations of carbonyl urethane and ester groups in the reference sample, and assuming [C=O]_{urethanes} = [C=O]_{esters}, the molar extinction coefficient ratio in the reference sample is

$$A_{ ext{C=Ourethanes}} / A_{ ext{C=O esters}} = \varepsilon_{ ext{urethanes}} / \varepsilon_{ ext{esters}} = 1.01 \cong 1$$

where $A_{C=0}$ is the absorbance of carbonyl urethane and ester groups in the reference sample and ε is the molar extinction coefficient of carbonyl urethane and ester groups in the reference sample.

The absorbance and relative concentration ratio is

$$A_{C=0 \text{ urethanes}}/A_{C=0 \text{ esters}}$$

= [C=0]_{urethanes}/[C=0]_{esters}
= 1.50 (calc value)

 $A_{\rm C=O urethanes} / A_{\rm C=O esters}$

$$= [C=0]_{urethanes}/[C=0]_{esters}$$
$$= 1.48 \quad (expl value)$$

where $A_{C=O}$ is the absorbance of the carbonyl urethane and ester groups in the polymer sample and [C=O] is the relative concentration of car-



Figure 3 Polymer I-P: (—) Fourier self-deconvoluted FTIR spectrum performed on the carbonylic band; (---) carbonylic band before deconvolution.

bonyl urethane and ester groups in the polymer sample.

¹H-NMR Spectroscopy

Figure 4 shows the ¹H-NMR spectrum and the signal assignment¹⁸ of polymer I-T. Note that the resonances that appear at 1.2, 3.1, 3.6, and 4.3 ppm are not due to a polymeric structure because of their narrowness. Such signals belong to solvent traces like *n*-BuOH; therefore, they were not taken into account in the spectrum analysis.

As can be seen on Figure 4, a partially polymerized structure is reached by the thermal curing method, because bands corresponding to vinyl protons still appear between 5.6 and 6.1 ppm.

To establish a quantitative analysis from such a spectrum, the area of TDI aryl protons (7.0-7.5 ppm) that are not involved in the polymerization process was selected as the internal standard.

Thus, the relationship between this selected internal standard and other resonances in the spectrum was calculated to find the relative ratio of m-DA : TDI : HEMA and elucidate the most presumable structure for functionalized precursor **V**. For this purpose two specific resonances were considered: the ones that correspond to one vinyl proton (6.1 ppm) and those belonging to methylenic nonvinyl protons (1.3– 1.7 ppm; i.e., total aliphatic methylene protons from the polymer).

According to this and considering each monomeric unit, if *a* is the area of TDI aryl protons (7.0-7.5 ppm), *b* is the area of one vinyl proton (6.1 ppm), *c* is the area of the total nonvinyl methylene protons (1.3-1.7 ppm), *x* is the number of total TDI aryl protons, *y* is the number of total vinyl protons = 1, and *z* is the number of total nonvinyl methylene protons, the following equation can be established:

$$a/x = b/y + c/z \tag{1}$$

On the assumption that the functionalized precursor V in Figure 4 (i.e., the ratio of m-DA : TDI : HEMA of 1 : 3 : 3) gives the monomer unit that appears on the spectrum, x = 9, y = 1 (already selected), and z = 18. Hence, from eq. (1),

$$a/9 = b + c/18 \tag{2}$$

Having measured the areas a, b, and c from the spectrum and doing the calculations, eq. (2) proves accurate, demonstrating that the values taken for x, y, and z were all correct.

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Figure 4 ¹H-NMR spectrum of polymer I-T.

Because a partially polymerized structure is reached by the thermal curing method, the ¹H-NMR technique gives useful data about the polymerization degree (PD) that this method allows. Thus, from the equation PD = 100 [vinyl protons/vinyl protons

+ methylene nonvinyl protons]

that is to say,



Figure 5 (—) TGA and (---) DTG curves for polymer I-P.

$$PD = 100[b/b + c] \tag{3}$$

It is inferred that about 50% of the functionalized monomer was polymerized.

FTIR and ¹H-NMR characterization studies on products (polymers I-T and I-P) would lead us to conclude that a ratio of m-DA : TDI : HEMA of 1 : 3 : 3 is mainly present on structure **V**.

On that account we may hypothesize that a structure labeled V in Figure 1 is one of the main products that behave like precursor bearing methacrylo-urethane capping groups.

TGA

Figure 5 shows the TGA and DTG curves plotted simultaneously as a result of the TGA performed on polymer I-P. The weight loss between 80 and 130°C can be attributed to solvent traces desorption. Up to 200°C no relevant changes occur, because the total weight loss reaches only about 10%. From 200 to 520°C the percentage increases quickly, but above 520°C the slope becomes rather smooth with a weight loss of 75%. An amount of 15% of solid residue is obtained due to the presence of an aromatic chemical structure.

The degradation rate versus temperature (DTG) curve shows a main two-stage process. The first stage falls between 213 and 378°C with a weight loss of 38% and the second between 406 and 529°C with a weight loss of 22%. The highest peaks correspond to 291, 323, and 421°C where the maximum degradation rates take place. There is no degradative process below 200°C, because a solvent desorption process is involved.

Optical Activity

Optical rotation measurements performed on polymer I-T gave a specific rotation $[\alpha]_D^{20}$ of 14.918°. Such a value shows the chirality found on this polymer, a property that could also be applied to polymer I-P, because the same molecular structure is present.

Influence of Curing Method on Properties of Obtained Polymers

As stated above, the thermal method leads to a soluble final product with a low crosslinking density. The photochemical method gave a highly crosslinked product, which was obtained within shorter exposure times than those required for the thermal curing.

Swelling indexes and swelling percentages on various solvents are listed on Table II. They were determined on the insoluble resin polymer I-P. As the table points out, this UV-cured resin is easily swollen in DMF and THF whereas no solvent retention occurs when it is tested in benzene, toluene, petroleum ether, or distilled water. Moreover, the low values for water give clear evidence of its hydrophobic behavior.

UV curing times and gel fraction percentage determined on the functionalized precursor V can be deduced from Figure 6. After 15 min of irradiation, about 25% of the gel fraction is attained. With a 60-min exposure about 80% gel content is obtained as a maximum value, showing a high conversion degree where no photoinitiator was

Table IIPolymer I-P Swelling Indexes (SI) andSwelling Percentage (SP) on Several Solvents

Solvent	SI^a	SP^{b}
Petroleum ether	1.0	0
Benzene	1.0	0
Toluene	1.0	0
Water	1.0	0
Ethyl acetate	1.6	22.2
Methanol	2.0	54.3
Acetone	3.1	81.1
Dioxane	3.3	ND^{c}
THF	4.2	ND^{c}
DMF	4.5	ND^{c}

^a SI = $V_{\rm S}/V_{\rm D}$, where $V_{\rm S}$ is the volume of the swollen gel and $V_{\rm D}$ is the volume of the dried gel.

^b SP = 100 $[(W_{\rm S} - W_{\rm D}]/W_{\rm D}$, where $W_{\rm S}$ is the weight of the swollen gel and $W_{\rm D}$ is the weight of the dried gel.

^c Swelling percentage could not be determined, because high swelling and very soft gels were obtained.



Figure 6 Gel percentage of UV cured films from functionalized precursor as function of irradiation time.

used. It was found that larger curing times than the ones used had no effect on increasing the obtained percent of gel content (80%).

CONCLUSIONS

A new functionalized acrylo-urethane polymer derived from *m*-DA was easily and successfully prepared. FTIR and ¹H-NMR studies demonstrated that it carries a ratio of *m*-DA : TDI : HEMA of 1 : 3:3.

The photocrosslinking studies showed a short curing time without using an initiator, which was probably due to the high value for functionality ($f \approx 3$) in precursor **V**. In addition, about 80% of the gel fraction was reached.

The final products (polymers I-T and I-P) showed good thermal stability and intrinsic chirality, which may confer specific application properties to them.

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