

# Synthesis of the Glycidyl Aniline Adduct and Its Crosslinking

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**ABSTRACT:** Synthesis of the adduct of aniline and glycidyl methacrylate and its polymerization and copolymerization with two diisocyanates are presented. Hexyl diisocyanate representing aliphatic compounds and toluene diisocyanate as the aromatic compound were used. UV and thermal initiations were applied. The curing process was controlled by FTIR analysis. Thermomechanical properties

of the compositions cured at different temperatures were compared. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 524–528, 2005

**Key words:** glycidyl aniline adduct; copolymerization; crosslinking; radical polymerization

## INTRODUCTION

In the past decade different acrylic and methacrylic polymers gained growing interest. An important group of these compounds is formed by copolymers. Diversity of acrylic and methacrylic polymers results from simple synthesis of various derivatives containing aliphatic, aromatic, cycloaliphatic, or more complicated fragments typical of enzymes, dyes, and drugs. A prospective group of acrylic polymers is formed by aminoacrylates. These compounds have been known since the 1930s but information about their first applications appeared in 1977.<sup>1,2</sup>

Aminoacrylates stored at 0°C for a long time polymerize spontaneously. The mechanism of their polymerization is the free radical. In the polymerization process a large amount of heat is released. An important drawback eliminating some applications is associated with the decrease of volume of the reacting mixture.<sup>2</sup>

Another group of methacrylic polymers is obtained in the addition reaction of diepoxide compound with difunctional amine.<sup>3–5</sup> Synthesis of these polymers was patented by Schlack.<sup>6</sup>

Primary monoamine or secondary diamine reacts with the epoxide groups of the diglycidyl compound. In this way hydroxyetheramine groups are formed characterized by high resistance to hydrolysis. These groups improve adhesion to glass, metals, and ceramics of the compounds due to intermolecular hydrogen and chelate bonds. Additionally, tertiary amine

groups can be transferred into the ionic form in the reactions with alkyl halogens or proton-containing acids.<sup>7</sup> The final thermoplastic product is soluble in organic solvents.

Recently Boutevin et al.<sup>8</sup> published a synthesis of multiacrylic resins from epoxy resins containing nitrogen atoms. These resins possess some advantageous characteristics including excellent reactivity. They have an epoxy backbone structure with the terminal unsaturated vinyl groups that can be cured by copolymerization with vinyl monomers, usually styrene or acrylic esters, analogous to the unsaturated polyesters.<sup>9–12</sup> Such materials have good adhesion to metals, low shrinkage, and good resistance to moisture. Their thermal characteristics are also promising.

This paper presents synthesis of a methacrylate derivative of epoxy resin containing nitrogen atoms. This compound was obtained in the addition reaction of glycidyl methacrylate to aniline. Then it was used for the preparation of polymers and copolymers with diisocyanates. Properties of the obtained polymers were studied.

## EXPERIMENTAL

### Materials

Glycidyl methacrylate,  $\alpha,\alpha'$ -azo-bis-isobutyronitrile, and hexyl diisocyanate were from Fluka (Switzerland), while toluene diisocyanate was from Sigma-Aldrich (Poznań, Poland). Aniline and xylene were from POCh (Gliwice, Poland). Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone) of the reagent grade was from Sigma-Aldrich. *tert*-Butylhydroquinone was bought from Merck (Schuchardt, Germany).

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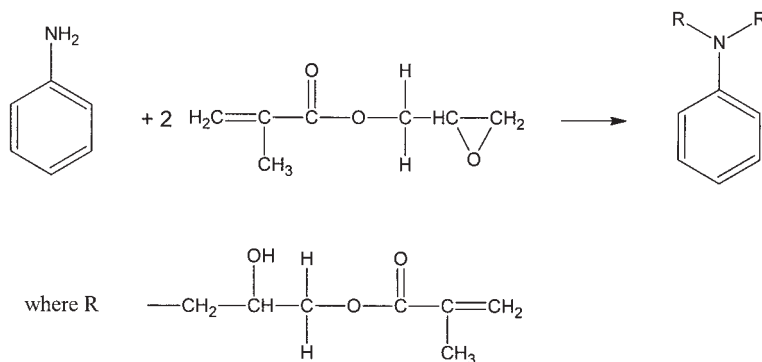


Figure 1 Synthesis of the adduct of aniline and glycidyl methacrylate.

### Synthesis of the adduct of aniline and glycidyl methacrylate

Glycidyl methacrylate in small portions was added to aniline heated to 60°C while stirring. The temperature of the reaction increased to 95–99°C and the mixture was maintained at this temperature for 6 h. The reaction was controlled by the change of epoxide number and FTIR analysis. The obtained adduct was crystallized from xylene. The final epoxide number of the product was 0.02.

The chemical structure of this compound was confirmed by elemental analysis. The following properties for this compound were also studied: epoxide number, viscosity, and refractive index (Table II).

### Curing procedure

The obtained adduct of aniline and glycidyl methacrylate was polymerized using 0.5%  $\alpha,\alpha'$ -azo-bis-isobutyronitrile or 2% Irgacure 651. Copolymers were obtained by dissolving the adduct in diisocyanates. The ratios of NCO/OH were 1:1 and 0.5:1 for both diiso-

cyanates studied. The solutions were deaerated with a vacuum dryer at 50°C.

Then the adduct and its solutions in diisocyanates polymerized using  $\alpha,\alpha'$ -azo-bis-isobutyronitrile were cured at 60, 70, 80, and 100°C for 1 h and then post-cured at 120° for 6 h. The adduct and its solutions were also polymerized by UV light. This curing was carried out for 4 h at room temperature and then the samples were postcured at 120° for 6 h.

Detailed recipes used in the syntheses are given in Table III.

### Properties of the polymers and copolymers

The infrared (IR) spectra were recorded on a FTIR Perkin–Elmer 2400 spectrometer using KBr pellets. The mass of the polymer and copolymer samples was always the same.

Thermal stability of the compositions was determined using a MOM derivatograph (Budapest, Hungary). The heating rate was 5°C/min in air. The initial decomposition temperatures were determined from the course of the  $T_G$  curves.

The calorimetric measurements were performed on a differential scanning calorimeter, Netzsch DSC 2000 (Netzsch, Germany). The conditions were as follows: sample weight ~10 mg, nitrogen atmosphere, sealed aluminum pans. An empty aluminum pan was used as a reference. The compositions were heated from 25 to 250°C at a heating rate of 10 K/min.  $T_g$  values were taken from the second DSC run.

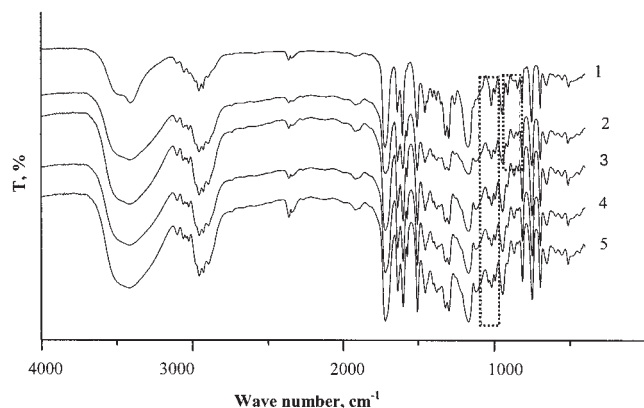


Figure 2 FTIR spectra for the glycidyl aniline adduct obtained after 1 h (1); 2 h (2); 3 h (3); 4 h (4); and 6 h (5) of the reaction.

TABLE I  
Elemental Analysis of the Studied Adduct

$\text{C}_{20}\text{H}_{27}\text{NO}_6$	Concentration, %			
	C	H	N	O
Assumed	63.64	7.23	3.71	25.42
Real	63.82	7.33	3.71	25.14

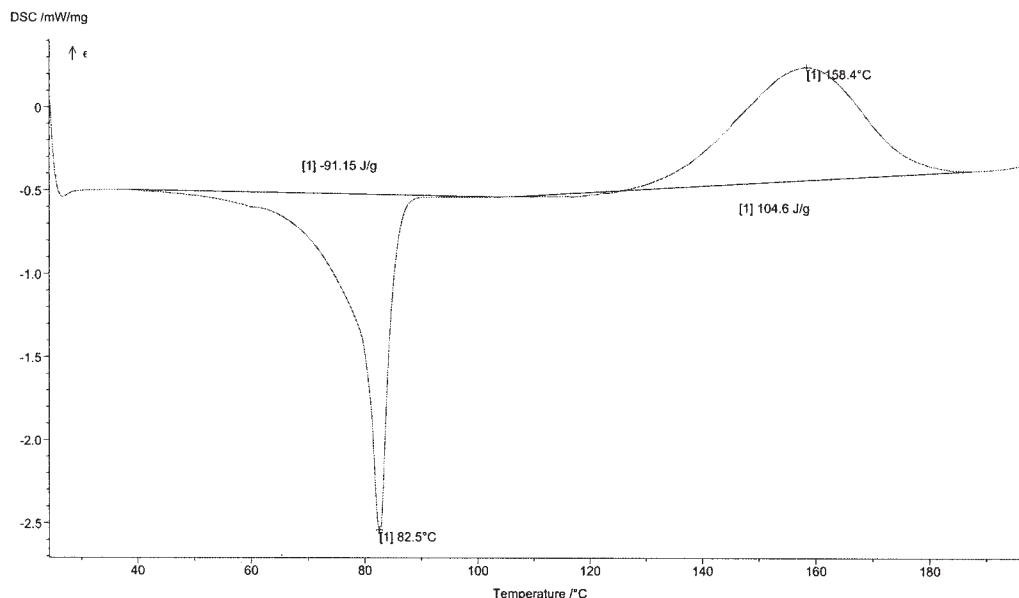


Figure 3 DSC analysis for the studied adduct.

Mechanical properties were determined according to the Polish Standards: flexural strength (PN-89/C-89,027), breaking strength (PN-81/C-89,034), elongation at break (PN-81/89,034), and Young modulus (PN-82/C-89,051) using the testing machine Zwick BT1-FROIOT.A50 (Roell, Germany), while head deflection temperature was determined using HDT3-Vicat (Ceast, Italy). Brinell hardness (PN-84/C-89,030) was measured with the Brinell tester.

## RESULTS AND DISCUSSION

Synthesis of the adduct of aniline and glycidyl methacrylate is presented in Figure 1. Its chemical structure was confirmed by FTIR and elemental analysis. In Figure 2 FTIR spectra made after 1, 2, 3, 4, and 6 h of the addition reaction are presented. From these spectra one can see that during the synthesis intensity of absorption band at  $3220\text{--}3420\text{ cm}^{-1}$  confirming formation of hydroxyl groups increases whereas the band at  $855\text{--}909\text{ cm}^{-1}$  decreases. The latter band of rather low intensity is typical for epoxide. The results from the elemental analysis are presented in Table I. By analyzing these data one can see that in the assumed and real chemical composition of this compound some discrepancies take place. The results from the DSC analysis presented in Figure 3 indicate that instead of crystallization this compound is not pure. The endothermic peak representing melting is wide. The melting temperature of this compound is  $82.5^\circ\text{C}$ . At larger temperatures the compound polymerizes. The exothermic peak with the maximum at  $158.4^\circ\text{C}$  confirms that a cured product is formed.

Other properties of the studied adduct are summarized in Table II. It is worth noticing that at  $25^\circ\text{C}$  its viscosity is rather high.

Detailed recipes used in the synthesis of cured products are presented in Table III. From these data one can see that polymers and copolymers with toluene diisocyanate and hexyl diisocyanate were prepared. Reactions were both thermally and UV initiated. Comparison of the thermomechanical properties of the obtained compositions is presented in Table IV. Polymers of glycidyl aniline adducts (Nos. 1 and 2) are extremely brittle, which causes preparation of forms that are very complicated. Both polymers are characterized by similar initial decomposition temperatures. The glass transition temperature for the polymer initiated by  $\alpha,\alpha'$ -azo-bis-isobutyronitrile is significantly higher while its HDT is the smallest. In comparison with sample 1 this material is even more brittle.

To improve mechanical properties of these compounds modifications with diisocyanates were carried out.<sup>14–16</sup> Of the obtained copolymers those containing toluene diisocyanate form an interesting group. Glass transition temperatures for copolymers 3 and 4 exceed  $170^\circ\text{C}$ . High values of hardness and small elongation

TABLE II  
Properties of the Adduct

Epoxide number, $L_{EP}$	0.02
Viscosity at $25^\circ\text{C}$ , mPas	21400
Viscosity at $40^\circ\text{C}$ , mPas	1710
Viscosity at $50^\circ\text{C}$ , mPas	540
Viscosity at $60^\circ\text{C}$ , mPas	210
Refractive index at $25^\circ\text{C}$	1.534

TABLE III  
Curing Recipe

Composition no.	Substrate, g				
	Adduct	Toluene diisocyanate	Hexyl diisocyanate	Irgacure 651	$\alpha,\alpha'$ -Azo-bis-isobutyronitrile
1	100	—	—	2	—
2	100	—	—	—	0.5
3	66.5	33.5	—	2	—
4	66.5	33.5	—	—	0.5
5	79.9	20.1	—	2	—
6	79.9	20.1	—	—	0.5
7	69.2	—	30.8	2	—
8	69.2	—	30.8	—	0.5
9	81.8	—	18.2	2	—
10	81.8	—	18.2	—	0.5

TABLE IV  
Thermomechanical Properties of the Obtained Compositions

Properties	Composition									
	1	2	3	4	5	6	7	8	9	10
Initial decomposition temperature, °C	270	270	280	280	280	280	270	270	270	270
Glass transition temperature, °C	125	143	174	176	119	132	101	102	105	102
HDT, °C	108	93	181	187	140	146	172	—	185	168
Breaking strength, MPa	41	20	26.5	23	27	26.5	—	—	27	—
Elongation at break, %	0.8	0.4	0.6	0.5	0.6	0.6	—	—	0.7	—
Young modulus, GPa	5.1	4.0	4.6	4.7	4.7	4.6	3.5	—	4.0	—
Flexural strength, MPa	118	84	109	83	90	86	145	—	140	139
Brinell's hardness, MPa	124	127	119	147	137	173	72	70	130	154
Brinell's hardness, MPa <sup>a</sup>	201	174	—	195	—	—	—	127	—	—

<sup>a</sup> For the samples heated at 180°C for 3 h.

at break confirm that these materials are highly crosslinked. The FTIR spectra for compositions 3 and 4 are presented in Figure 4. Unfortunately, in these spectra the bands at 814, 990, 1630, 3020, and 3085

$\text{cm}^{-1}$ , which are typical for unreacted vinyl groups, are visible.<sup>13</sup> The same bands are visible in the spectra of compositions 7 and 8, which contain hexyl diiso-

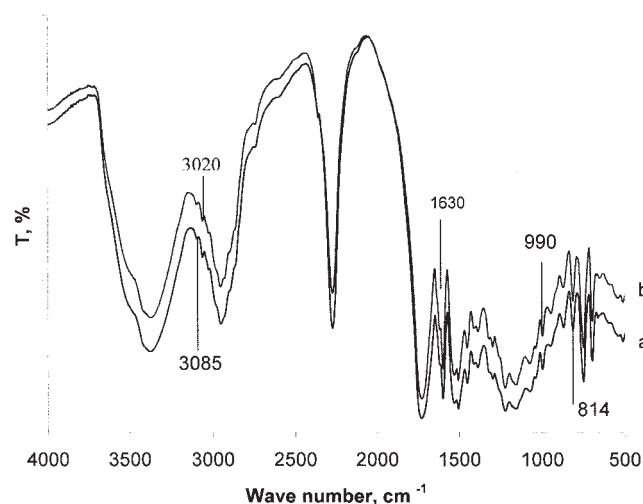


Figure 4 FTIR spectra for the glycidyl aniline adduct and toluene diisocyanate, composition 3, initiated by UV light (a), and composition No.4, initiated thermally (b).

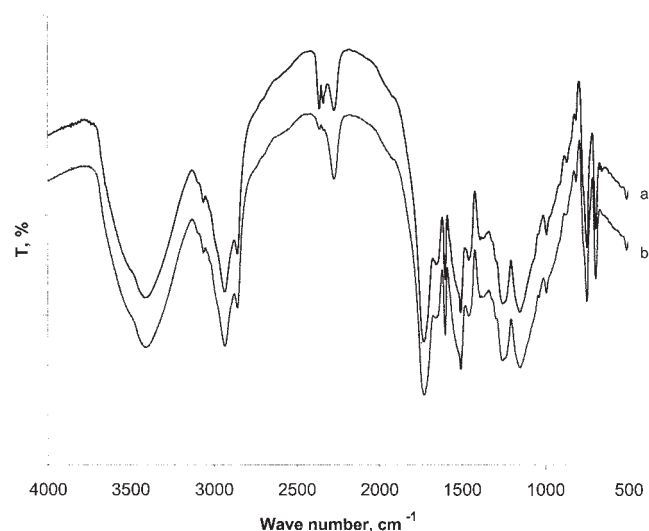
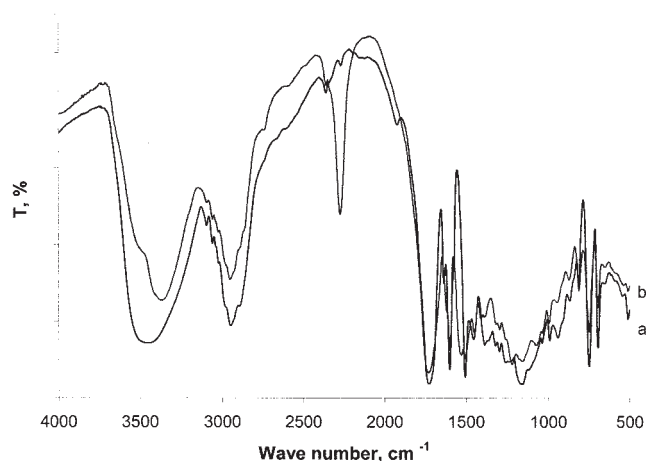


Figure 5 FTIR spectra for the copolymers of the glycidyl aniline adduct and hexyl diisocyanate, composition 7, initiated by UV light (a), and composition 8, initiated thermally (b).



**Figure 6** FTIR spectra for the samples postcured at 180°C, No.2 (a) and No. 4 (b).

cyanate (Fig. 5). This means that the process of curing is not finished at 120°C.

For this reason, samples 1, 2, 4, and 8 were additionally heated at 150 and 180°C for 3 h. In any case, heating at 180°C leads to an increase of Brinell's hardness (Table IV). The exemplary FTIR spectra for samples 2 and 4 (Fig. 6) show that heating at 180°C causes a decrease in intensity of the bands corresponding to vinyl bonds but the band still exists in the chemical structure of the polymer of glycidyl aniline adduct and its copolymer with diisocyanate. Probably some steric effects are responsible for such a course of these reactions.

The results presented here indicate that polymers of glycidyl aniline adducts are extremely brittle. Their copolymers with diisocyanates have better mechanical properties. Their polymerization can be initiated by UV light or thermally. In both types of the obtained polymers unreacted vinyl bonds are presented in their

structures. Even postcuring at high temperatures does not cause their disappearance.

## CONCLUSIONS

Synthesis of the adduct of aniline and glycidyl methacrylate is presented. Unfortunately, polymerization of this compound led to a very brittle product. Its copolymers with diisocyanates had better mechanical properties.

In the chemical structure of the obtained compositions unreacted vinyl bonds were detected. Even postcuring at high temperatures did not cause their disappearance.

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