

Synthesis of Glycidyl Amine Adducts and Their Copolymerization with Glycidyl Methacrylate

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ABSTRACT: Syntheses of new adducts from glycidyl methacrylate and the following amines: aniline, *p*-phenylenediamine, 4,4'-oxydianiline, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfone, 4,4'-thiodianiline, and 4,4'-diaminodicyclohexylmethane, are presented. These adducts were copolymerized with glycidyl methacrylate. The curing process was initiated thermally and by UV light.

Thermomechanical properties of the obtained compositions were studied. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2461–2466, 2005

Key words: glycidyl amine adduct; copolymerization; crosslinking; radical polymerization

INTRODUCTION

In the past decade different acrylic and methacrylic polymers have gained growing interest. A prospective group of acrylic polymers is formed by aminoacrylates. These compounds are formed in the reactions of aliphatic or aromatic amines with epoxide groups of glycidyl compounds. As a result, hydroxyetheramine groups are created, which enhance adhesion of the obtained adducts to glass and metals and are responsible for interactions between molecules. These adducts are characterized by high reactivity and viscosity and have a tendency toward spontaneous polymerization.¹ Crosslinked products are obtained due to a side reaction of epoxides with secondary hydroxyl groups. Basic substances like soda, sodium methacrylate, or tertiary amines act as etherification catalysts.^{2,3}

The first concept of linear nitrogen-containing polymers obtained by the addition of diepoxides and amines having two active hydrogen atoms was outlined as early as 1934 by Schlack in the first patent of epoxy resins chemistry.⁴

Boutevin et al.⁵ published the 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 terminal unsaturated vinyl groups that can be cured by copolymerization with vinyl monomers, usually styrene or acrylic esters, analogous to the unsaturated polyesters.^{6–9} Such ma-

terials have good adhesion to metals, low shrinkage, and good resistance to moisture. Their thermal characteristics are also promising. Unfortunately, aniline and its derivatives are classified as toxic substances, which can cause health troubles in workers when they are improperly handled. According to the U.S. Environmental Protection Agency, aromatic amines are suspected of mutagenic properties, even at very low concentrations.¹⁰

In our previous paper¹¹ we presented the 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 preparation of polymers and copolymers with diisocyanates.

This paper presents the synthesis of some new adducts from glycidyl methacrylate and the following amines: aniline, *p*-phenylenediamine, 4,4'-oxydianiline, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfone, 4,4'-thiodianiline, and 4,4'-diaminodicyclohexylmethane. Their copolymerizations with glycidyl methacrylate were studied. UV and thermal initiations were applied.

EXPERIMENTAL

Materials

Glycidyl methacrylate, 4,4'-oxydianiline, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodicyclohexylmethane, and α,α' -azobisisobutyronitrile were reagent grade from Fluka (Switzerland). Aniline from POCh (Gliwice, Poland) was purified by distillation. Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone), *p*-phenylenediamine, and 4,4'-thiodianiline were from Sigma–Aldrich (Poznań, Poland), while *tert*-

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TABLE I
Conditions of the Synthesis of Amine Adducts

Adduct No.	Monomers		Mole ratio (A:GM)	Synthesis conditions	
	Amine (A)	Epoxide compound (GM)		Reaction time, h	Temp., °C
1	Aniline	Glycidyl methacrylate	1 : 2	7	97–98
2	4,4'-Oxydianiline	Glycidyl methacrylate	1 : 4	4	96–98
3	4,4'-Diaminodiphenylmethane	Glycidyl methacrylate	1 : 4	5	98–100
4	4,4'-Diaminodicyclohexylmethane	Glycidyl methacrylate	1 : 4	5	96–99
5	4,4'-Diaminodiphenylsulfone	Glycidyl methacrylate	1 : 4	31	96–98
6	4,4'-Thiodianiline	Glycidyl methacrylate	1 : 4	9	97–100
7	<i>p</i> -Phenylenediamine	Glycidyl methacrylate	1 : 4	2	96–100

butylhydroquinone was from Merck (Schuchardt, Germany).

Preparation of the adducts

Seven adducts containing glycidyl methacrylate and different amines were prepared. The detailed recipes used in these studies are given in Table I.

All reactions were performed in a glass reactor equipped with a stirrer and a thermometer. The typical procedure was as follows: glycidyl methacrylate in small portions was added to amine heated up to 60°C while stirring. Temperature of the reaction increased to 96–100°C. The mixture was maintained at this temperature for 2–31 h. The addition reaction proceeded in the presence of the inhibitor *tert*-butylhydroquinone. Its concentration was 0.01% except for an adduct containing *p*-phenylenediamine, when its amount was 0.03%.

The reactions were controlled by change of epoxide number, FTIR, and elemental analyses. The following properties for these compounds were also studied: epoxide number, viscosity, refractive index, and initial decomposition temperature.

Curing procedure

Copolymers of the obtained adducts and glycidyl methacrylate were cured by two methods of radical polymerizations: thermally using 0.5% wt α,α' -azobisisobutyronitrile and with UV light using 2% wt Irgacure 651.

Copolymers were obtained by dissolving the adducts in glycidyl methacrylate. The ratios of vinyl groups of the adducts to vinyl groups of glycidyl methacrylate were 1 : 1 and 1 : 0.5. The homogeneous mixtures were deaerated with a vacuum dryer at 50 °C.

Their solutions in glycidyl methacrylate polymerized using α,α' -azobisisobutyronitrile were cured at 60 °C for 20 h, at 70, 80, and 100 °C for 1 h, at 120 °C for 6 h, and then postcured at 150 °C for 6 h. UV crosslinking of these products was carried out for 4 h

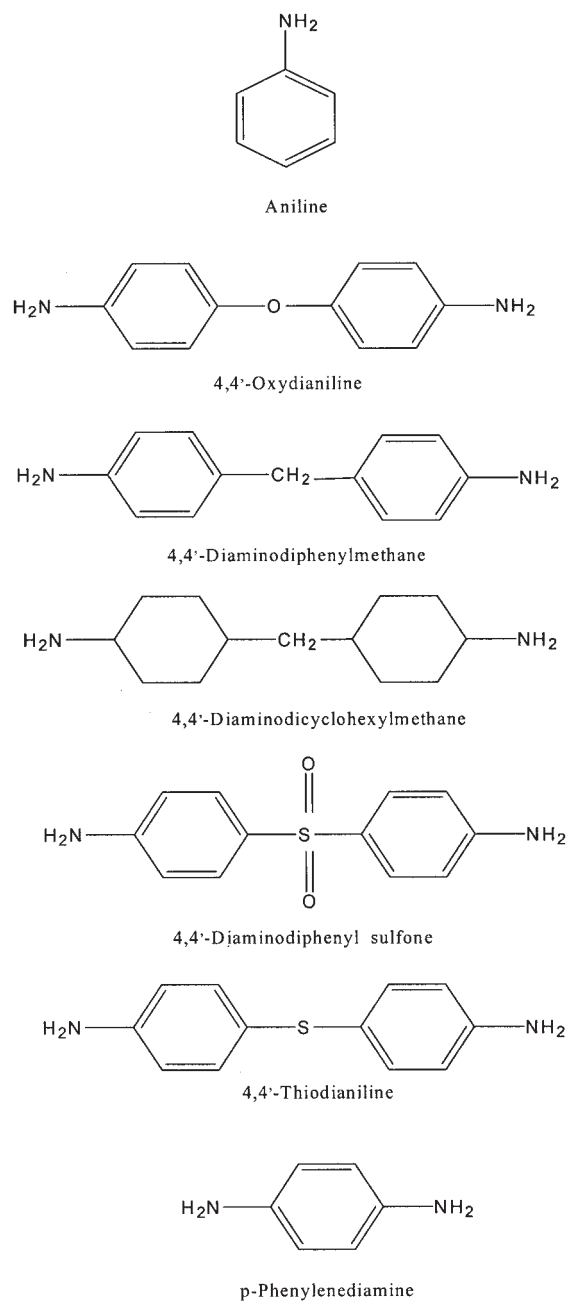


Figure 1 Chemical structure of the amines used.

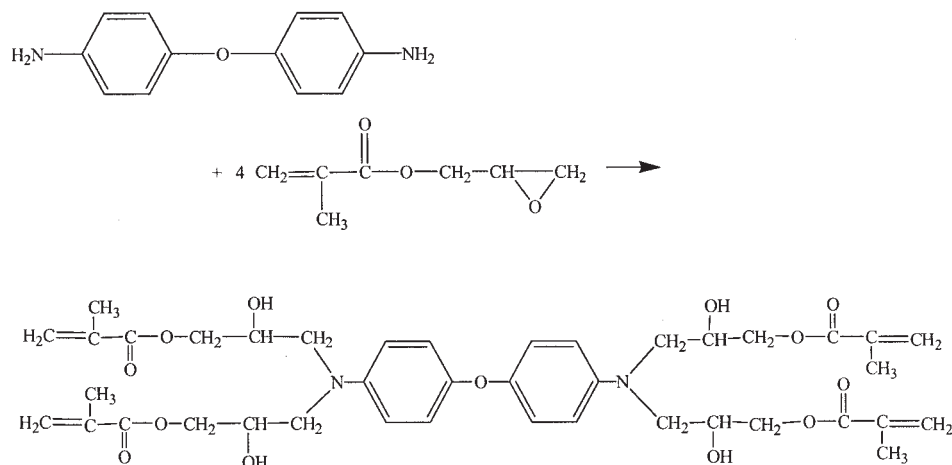


Figure 2 Synthesis of the adduct 4,4'-oxydianiline and glycidyl methacrylate.

at room temperature and then the samples were post-cured at 120°C for 6 h and at 150°C for 6 h. Only copolymers of the *p*-phenylenediamine adduct were not postcured at 150°C, because at this temperature all samples cracked.

Properties of the copolymers

The infrared (IR) spectra were recorded on a FTIR Perkin-Elmer 2400 spectrometer using KBr pallets. The mass of the 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.

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. As the second DSC runs were linear for all studied copolymers, de-

termination of their glass transition temperatures was not possible.

Mechanical properties were determined according to the Polish Standards: flexural strength (PN-89/C-89,027) and elastic modulus (PN-82/C-89,051) using the testing machine Zwick BT1-FROIOT.A50 (Roell, Germany). The deflection temperature (HDT) was determined using HDT3-Vicat (Ceast, Italy). Brinell hardness (PN-84/C-89,030) was measured with a Brinell tester.

RESULTS AND DISCUSSION

In the previous paper we presented the synthesis and properties of the copolymers based on the adduct of aniline and glycidyl methacrylate. Following this work we synthesized a range of different amine glycidyl adducts. Chemical structures of the amines used for their preparation are presented in Figure 1. The studied amines have aromatic character except for 4,4'-diaminodicyclohexylmethane. The detailed synthesis conditions of the adduct based on the above-mentioned amines and glycidyl methacrylate are presented in Table I. All of these compounds were prepared in stoichiometric reactions. The exemplary

TABLE II
Properties of Glycidyl Amine Adducts

Adduct No.	Viscosity at 50°C (mPas)	Refractive index at 25°C	Epoxide number (L_{Ep})	Color	Initial decomposition temperature (°C)
1	1140	1.5340	0.02	Rosy	280
2	35760	1.5549	0.02	Light rosly	330
3	167340	1.5558	0.02	Light yellow	320
4	>600000	1.5096	0.03	Red	250
5	9890	1.5645	0.04	Rosy	285
6	220750	—	0.02	Brown	300
7	14400	1.5350	0.02	Black	320

TABLE III
Elemental Analysis of the Studied Adducts

Adduct No.	Theoretical (%)			Measured (%)		
	C	H	N	C	H	N
1	63.64	7.23	3.71	63.72	7.33	3.71
2	62.48	6.83	3.64	62.37	6.86	3.75
3	64.21	7.11	3.65	63.95	6.98	3.66
4	63.21	8.56	4.10	63.05	8.61	3.89
5	59.25	6.43	3.30	59.10	6.43	3.42
6	61.20	6.69	3.56	61.31	6.82	3.36
7	60.33	7.16	4.14	60.19	7.19	3.83

synthesis of the adduct of 4,4'-oxydianiline and glycidyl methacrylate is shown in Figure 2. The amounts of reagents were chosen in such a way that 2 mol of glycidyl compound reacted with 1 mol of amine. In the case of diamines 4 mol of glycidyl methacrylate was used.

It should be noted that the times of addition reactions are different. In the case of the adduct based on *p*-phenylenediamine, the reaction lasted the shortest time (2 h), while for the adduct with 4,4'-diaminodiphenyl sulfone the reaction ran 31 h. For other amines the reaction times changed from 4 to 9 h, meaning that the amines used for preparation of the adducts indicate different reactivities toward glycidyl methacrylate. Among them the most reactive is *p*-phenylenediamine, while 4,4'-diaminodiphenyl sulfone is the least active.

Properties of the obtained adducts are summarized in Tables II and III. From these data one can see that the obtained adducts are compounds of rather high viscosity. Only the adduct based on aniline representing monoamines is less viscous. All obtained compounds are colorful.

Chemical structures of the obtained adducts were confirmed by FTIR and elemental analyses. In Figure 3 FTIR spectra made after 1, 2, and 5 h of the addition

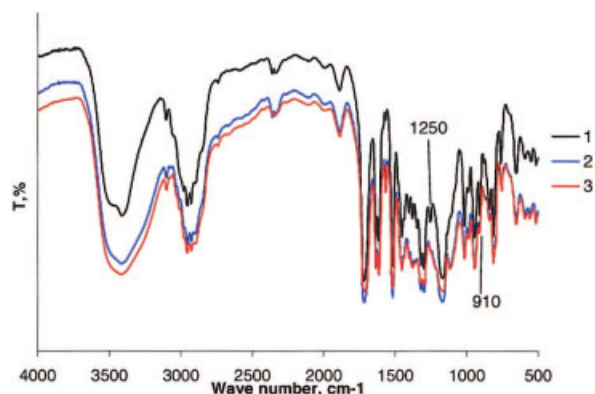


Figure 3 FTIR spectra for the glycidyl 4,4'-diaminodiphenylmethane adduct obtained after 1 h (1), 2 h (2), and 5 h (3) of reaction.

TABLE IV
Synthesis Recipe

Composition No.	Substrate (mol)							GM
	Adduct No.							
	1	2	3	4	5	6	7	
1a	1							1
1b	1							2
1c	1							1
1d	1							2
2a		1						2
2b		1						4
2c		1						2
2d		1						4
3c			1					2
3d			1					4
4a				1				2
4b				1				4
4c				1				2
4d				1				4
5a					1			2
5b					1			4
6c						1		2
6d						1		4
7c							1	2
7d							1	4

a, b: copolymers crosslinked by UV light; c,d: copolymers crosslinked thermally.

reaction between 4,4'-diaminodiphenylmethane and glycidyl methacrylate are presented. From these spectra one can see that during the synthesis the intensity of the absorption band at 3220–3420 cm^{-1} , confirming formation of hydroxyl groups, increases while the bands of epoxide groups at 910 and 1250 cm^{-1} decrease or even disappear. After 2 h of reaction the band at 1250 cm^{-1} representing stretching vibrations of epoxides disappears completely. The chemical structures of the obtained adducts were also confirmed by elemental analysis. The data in Table III

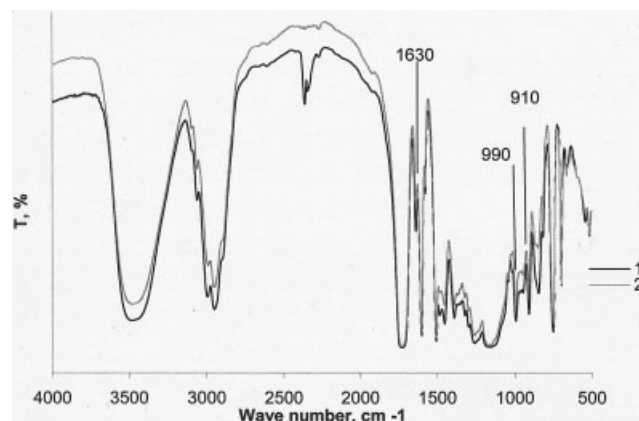


Figure 4 FTIR spectra for the copolymers of the glycidyl aniline adduct and GM; composition 1b, initiated by UV light (1) and then postcured at 150 °C (2).

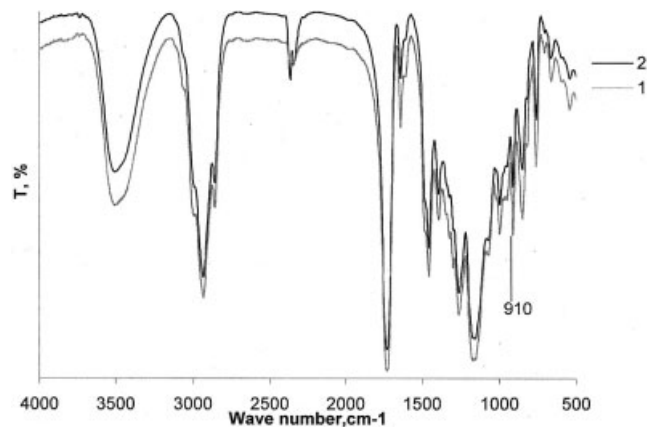


Figure 5 FTIR spectra for the copolymers of the glycidyl 4,4'-diaminodicyclohexylmethane adduct and GM; composition 4b, -initiated by UV light (1) and then postcured at 150 °C (2).

show that the assumed and actual chemical compositions of these compounds are very similar.

As the obtained adducts are capable of spontaneous polymerization and are characterized by rather high viscosities, preparation of their homopolymer samples in the molds was complicated. The adducts were also characterized by limited solubility in popular vinyl monomers. For these reasons glycidyl methacrylate as a good solvent for all the studied adducts was used for preparation of their copolymers. Copolymerization reactions were initiated both thermally and by UV light.

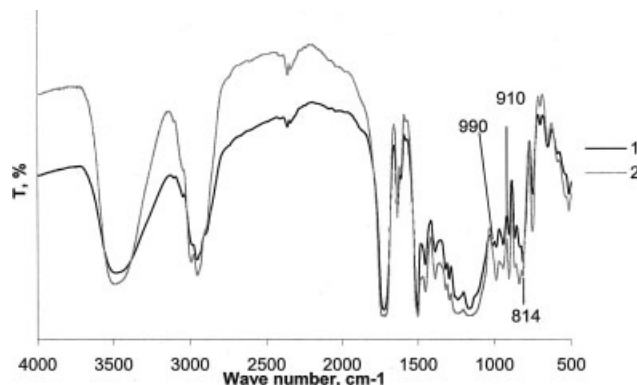


Figure 6 FTIR spectra for the copolymers of the glycidyl 4,4'-oxydianiline adduct and GM; compositions 2c (1) and 2d (2) were cured thermally.

The list of synthesized copolymers is presented in Table IV. Copolymers of different chemical structures were obtained by changing the molar ratio of adduct/glycidyl methacrylate. The properties of the products polymerized in the presence of chemical initiator α,α' -azobisisobutyronitrile and UV light are compared.

Figure 4 presents the FTIR spectra for the composition 1b, initiated by UV radiation and then postcured at 150 °C. After postcuring intensities of absorption bands at 1630, 990, and 814 cm^{-1} , which are characteristic of vinyl groups, decrease but peaks do not completely disappear. For the compositions containing larger amounts of glycidyl methacrylate a similar situation is observed, but in these cases the bands at

TABLE V
Thermomechanical Properties of Obtained Compositions

Composition No.	Initial decomposition temperature (°C)	HDT (°C)	Flexural strength (MPa)	Elastic modulus (GPa)	Brinell's hardness (MPa)	Brinell's hardness (MPa ^a)
1a	245	122	88	5.3	154	195
1b	245	118	99	5.0	150	184
1c	245	125	112	5.4	152	195
1d	248	120	123	5.1	156	184
2a	230	183	103	5.0	125	189
2b	232	160	107	4.9	136	178
2c	210	172	101	4.9	126	175
2d	227	157	100	5.0	139	176
3c	210	166	87	4.9	149	156
3d	258	175	98	4.6	142	160
4a	253	184	80	4.2	136	156
4b	240	178	62	4.4	130	164
4c	233	187	96	4.4	136	156
4d	230	177	86	4.1	130	162
5a	218	190	107	5.0	126	180
5b	244	225	81	4.9	136	183
6c	210	180	93	5.0	149	174
6d	260	193	65	4.6	135	178
7c	257	135	63	3.2	178	—
7d	230	103	65	3.1	174	—

^aFor samples postcured at 150°C.

910 cm^{-1} typical of epoxide rings are additionally visible (Fig. 5). In Figure 6 the FTIR spectra for compositions 2c and 2d, which were thermally polymerized, are presented. In these spectra unreacted vinyl groups are also visible, independent of the molar ratio of the glycidyl methacrylate to the adduct used. The band at 910 cm^{-1} indicates that the composition containing larger amounts of glycidyl methacrylate possesses unreacted epoxide groups.

The comparison of the thermomechanical properties of the obtained compositions is presented in Table V. Generally all the compositions are characterized by high initial decomposition and deflection temperatures. Only the compositions based on aniline and *p*-phenylenediamine adducts have smaller HDT values, but their initial decomposition temperatures are similar to those of the other studied compounds. In most cases copolymers with higher density of crosslinking possess higher deflection temperatures. Flexural strengths are the highest for copolymers based on the adducts of 4,4'-oxydianiline, while they are lowest for the copolymer of 4,4'-diaminodicyclohexylmethane glycidyl adduct and glycidyl methacrylate. Insignificantly larger values characterize the copolymers based on *p*-phenylenediamine adduct. Copolymers of *p*-phenylenediamine adduct and glycidyl methacrylate are additionally characterized by the largest values of hardness. The others achieve similar hardness after additional curing at 150°C.

High values of hardness observed for these copolymers suggest a large arrangement of their molecular structures.

CONCLUSIONS

The series of new copolymers prepared from glycidyl amine adducts and glycidyl methacrylate is presented. Due to high crosslinking degrees these materials are characterized by high thermal stabilities. Simultaneously they are extremely hard.

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