

Synthesis and Reactivity of Mannich-Derived Polyoxyethylene Amines as Epoxy Curing Agents

J. J. LIN, G. P. SPERANZA,* H. G. WADDILL*

Department of Chemical Engineering, National Chung-Hsing University, Taichung 402, Taiwan, Republic of China

Received 10 April 1997; accepted 1 July 1997

ABSTRACT: The facile Mannich reaction of phenol, formaldehyde, and polyoxyalkylene polyamines at various molar ratios afforded a family of polyetheramines containing functionalities of phenol, primary amines, secondary amines, and polyoxyethylene or polyoxypropylene block copolymers in the same molecule. The synthesis can be generalized by using various polyoxyethylene or polyoxypropylene diamines (and triamines) of molecular weights ranging from 104 to 430 to prepare a family of Mannich amines, with exception of certain gel products such as phenol/formaldehyde/bis(aminoethyl)ether adduct at 1 : 3 : 3 molar ratio. The series of Mannich amines were evaluated for their epoxy curing reactivities by comparing their gel time and drying time. The Mannich amines prepared from polyoxyethylene amines exhibited higher reactivities than those of polyoxypropylene amine derivatives. The trend of their relative reactivities is explained by the molecular size, the multiplicity of amines in the molecule, and the steric hindrance of amine structure. The physical properties of cured epoxy materials, such as impact, tensile, flexural strength, and hardness properties were also measured and correlated with the amine molecular weight, crosslinking density, and the presence of phenol group. The structure–property relationship is discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2339–2346, 1997

Key words: Mannich; polyoxyethylene; polyoxypropylene; amine; epoxy curing

INTRODUCTION

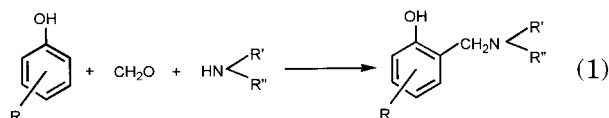
The Mannich condensation of phenols, formaldehyde, and amines [eq. (1)], first reported as early as 1942,¹ are versatile for many industrial applications.^{2,3} The uses of various amines and alkylphenols gave rise to different Mannich products that are useful for fine chemicals,^{4,5} polymers,^{6–8} grease components,⁹ antifoulants,¹⁰ fuel additives,^{11,12} etc. The versatility comes from the diversity of the functional groups in Mannich con-

densates. For example, one variation of Mannich condensates that contains functionalities of rigid phenols and multiple hydroxy groups from diethanolamines was suitable for making rigid polyurethane foam.¹³ In epoxy applications, the presence of phenol groups in Mannich condensates may have advantages in terms of providing further reactive sites and also as acceleration catalyst,^{14–16} as it is known that phenol-containing compounds, such as poly(*p*-vinylphenol) or 2,3,6-tris(dimethylaminomethyl)phenol, can function as epoxy curing accelerators.^{17,18}

Correspondence to: J. J. Lin.

* Retired from Texaco Chemical Co., P.O. Box 15730, Austin, TX 78761.

Journal of Applied Polymer Science, Vol. 66, 2339–2346 (1997)
© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/122339-08



Furthermore, Mannich condensation can convert the low molecular weight of polyoxyalkylene amines into the corresponding prepolymers that are more suitable for epoxy curing, because the low molecular weight amines as epoxy curing agents usually generate too high a crosslink density of brittle materials. In some cases, the cured materials show an undesired cloudy tacky surface.¹⁵ Those disadvantages may be overcome by using the higher molecular weight analogs. Previously, we reported such an approach that a low molecular weight of polyoxyethylene diamine was coupled into the higher molecular weight of analogs through carboxylic acid-derived amide linkages.¹⁹ In this article, we reveal the preparation of a series of novel Mannich condensates from low molecular weight and highly active oxyethylene amines, as well as their relative reactivities towards epoxy curing. The use of these Mannich amines has two immediate advantages with respect to the chemical reactivities toward epoxy curings: (1) the high curing activity due to the oxyethylene-terminating amine structure, and (2) the existing phenol groups, which provide a balanced rigidity to the cured polymers.

EXPERIMENTAL

Synthesis of Mannich Amines

The typical experimental procedures for synthesizing Mannich amines are described: to a 2-L three-necked flask (equipped with mechanical stirrer, nitrogen inlet, thermometer, Dean-Stark trap, and dropping funnel) were placed with phe-

nol (188 g, 2.0 mmol) and triethylene glycol diamine (Jeffamine[™] EDR-148, from Huntsman Chemical Co., 296 g, 2.0 mmol). While stirring, 37% formalin (162 g, 2.0 mmol) was added over a 1 h and 23 min period of time. During the addition, the exothermic temperature up to 45°C was observed. The mixture was stirred for additional 2 h at approximately 28°C and then heated to 80°C and held at that temperature for 3 h. The temperature was raised to 120–130°C to remove most of the water. The remaining water was removed at 120°C under a water aspirator vacuum. The final product was a clear yellow, water-soluble liquid, having an amine content of 7.91 mEq/g (calc. 7.87 mEq/g) and ¹H nuclear magnetic resonance (NMR) (CDCl₃, 300 MHz) 6.7–7.2(4H, m), 4.0(2H, m), 3.5–3.6(8H, m), and 2.8–2.9(4H, m). Using the same experimental procedures, a series Mannich condensates, as indicated by the representative structure in eq. (2) and also in Tables I, II, III, and IV, were prepared from bis(aminoethyl) ether (BAEE), triethyleneglycol diamine (Jeffamine[™] EDR-148), tetraethyleneglycol diamine (Jeffamine[™] EDR-192), polyoxypropylene diamines (x = 2.6, Jeffamine[™] D-230 and x = 5.6, D-400) and polyoxypropylene triamine (x + y + z = 5.3, Jeffamine[™] T-403), at various phenol/amine/formaldehyde molar ratios. These starting amines were available from Huntsman Co. with structures shown in Figure 1. When 1 mol phenol was reacted with 3 mol of formaldehyde and 3 mol of bisaminoethyl ether or 3 mol of triethyleneglycol diamine, the results were gel products that were not suitable for epoxy resin applications. A gel product was also formed when 4 mol of phenol

Table I Comparison of Amine Reactivity During Epoxy Curing Process: Mannich Amines Containing Polyoxyethylene Amines and Polyoxypropylene Amines

Condensates ^a of Phenol/Amine (IIa–f)	Phenol/CH ₂ O/Amine Molar Ratio	Gel Time (min)	Set-to-Dry (h)	Drying Time, 6-mil Film	
				Surface Dry (h)	Thru-Dry (h)
a. BAEE	1/1/1	13.2	1.1	2.7	—
b. Jeffamine [®] EDR-148	1/1/1	15.6	2.0	3.1	—
c. Jeffamine [®] EDR-192	1/1/1	19.2	3.7	5.1	11
d. Jeffamine [®] D-230	1/1/1	128	9.0	16	29
e. Jeffamine [®] D-400	1/1/1	—	23.8	38	54
f. Jeffamine [®] T-403	1/1/1	132	9.0	13	17

^a Condensates of phenol/formaldehyde/amine (IIa–f) at 1 : 1 : 1 molar ratio.

Table II Properties of Epoxy Resin Systems Cured with Phenol-Formaldehyde-BAEE Condensates

	Example	
	1	2
Formulation		
Epoxy resin, ^a pbw	100	100
Phenol/CH ₂ O/BAEE, ^b pbw		
Molar ratio: 1/1/1	38	—
1/2/2	—	30
Brookfield Viscosity, cps, 25°C	8500	20000
Gel time, min (200 g mass)	13.2	26.6
Peak exothermic temperature, °C	227.5	238.0
Time to peak temp., min	22.0	37.2
Properties of cured 1/8-in casting ^c		
Rheometric impact, total energy, in-Ib	26	18
Tensile strength, psi	10100	9900
Tensile modulus, psi	459000	399000
Elongation at break %	9.0	6.1
Flexural strength, psi	15900	17200
Flexural modulus, psi	452000	409000
HDT, °C, 264 psi/66 psi	75/79	107/113
Shore D hardness, 0–10 s	81–79	83–81
Compression strength at yield, psi	12,900	13,400
at failure, psi	41,200	40,100
% Compression at peak	60.0	53.6
% Weight gain, 24 h water boil	2.4	1.9
3 h acetone boil	3.3	0.8
Adhesive properties ^d		
Tensile shear strength, psi	2800	2000
T-peel strength, pli	4.2	3.9

^a Diglycidyl ether of bisphenol A, epoxy equivalent weight 185–192.

^b Mannich condensates of phenol-formaldehyde-bis(aminoethyl)ether at 1 : 1 : 1 or 2 : 2 : 2 molar ratio.

^c Cured 2 h 80°C, then 3 h 150°C.

^d Cured 1 h 150°C.

and 4 mol of formaldehyde were reacted with 1 mol of triethyleneglycol diamine.

Epoxy Resin Curing

The preparation of a cured epoxy resin is carried out in the following manner: diglycidyl ether of bisphenol A (Shell Product, Epon 828, with an epoxide equivalent weight of ca. 185), was used without dilution or other additives. The epoxy resin and an equivalent amount of the Mannich amines were mixed, degassed through application of a vacuum, and poured into 1/8"-thick aluminum molds. For the film system, the sample was

dip coated and cured on a steel plate. The curing conditions were indicated in the tables. The mixtures were usually cured at 80°C for 2 h plus 150°C for 3 h, in some cases 150°C for 1 h. After curing, the cured materials are cut into test samples. The following properties were measured.

Drying time: A reproducible determination of various stages and rates of film formation in drying and curing of organic coatings. A Gardner Circular Drying Time Recorder (Gardner Laboratories, Bethesda, MD) was used.

Impact: As measured by Gardner impact, according to ASTM D2794-69(1974). A known weight was allowed to fall from a measured height

Table III Properties of Epoxy Resin Systems Cured with Phenol-Formaldehyde-Triethylene Glycol Diamine Condensates

	Example	
	3	4
Formulation		
Epoxy resin, ^a pbw	100	100
Phenol/CH ₂ O/amine condensate, pbw		
Molar ratio: 1/1/1	45	—
1/2/2	—	28
Brookfield viscosity, cps, 25°C	6500	7500
Gel time, min (200 g mass)	15.6	39.4
Peak exothermic temperature, °C	210.0	218.5
Time to peak temp., min	20.5	55.7
Properties of cured 1/8-in casting ^b		
Rheometric impact, total energy, in-lb	40	22
Tensile strength, psi	10000	10200
Tensile modulus, psi	486000	472000
Elongation at break %	9.5	6.4
Flexural strength, psi	17300	16700
Flexural modulus, psi	469,000	449,000
HDT, °C, 264 psi/66 psi	67/69	74/81
Shore D hardness, 0–10 s	81–79	81–78
Compression strength at yield, psi	12400	12500
at failure, psi	48,100	37,600
% Compression at peak	65.0	60.4
% Weight gain, 24 h water boil	2.8	3.0
3 h acetone boil	3.8	3.8
Adhesive properties ^c		
Tensile shear strength, psi	3700	3700
T-peel strength, pli	4.3	4.0

^a Diglycidyl ether of bisphenol A, epoxy equivalent weight 185–192.

^b Cured 2 h 80°C, then 3 h 150°C.

^c Cured 1 h 150°C.

to exert a certain force upon a film sample by means of a round-nose punch. After striking, the film is examined for damage.

Tensile shear strength, ASTM D 1002: Strength properties, in psi, of an adhesive when loaded to produce shear distortion of planes parallel to the plane of the adhesive bond.

T-peel strength, pli, ASTM D 1876: A test made on bonded strips of metals by peeling the metal strips back and recording the adhesive strength values. Other test methods based on ASTM are cited in the following: gel time (min), ASTM D-2471–71; Shore D-Hardness 0–10 s, ASTM D-2240; elongation at break, ASTM D-638; heat deflection temperature (HDT) (°C, 264 psi/66 psi), ASTM D-648; tensile strength (psi), ASTM D-638; flexural strength (psi), ASTM D-790; flexural modulus (psi), ASTM D-695; compres-

sion strength at yield and at failure (psi), ASTM D-695.

RESULTS AND DISCUSSION

Synthesis of Mannich Amines

Under either acidic or basic conditions, the reaction of formaldehyde and phenol is well known to form predominant *o*- and *p*-methylolphenol epoxy novolacs intermediate.^{3,20} In the presence of primary amines and without catalyst, analogous reaction mechanism leads to the formation of secondary amine with methylene linkage to phenol. Autocatalyzed by amine substrates, the Mannich reaction is straightforward for adding amine func-

Table IV Properties of Epoxy Resin Systems Cured with Phenol-Formaldehyde-Tetraethylene Glycol Diamine Condensates

	Example		
	5	6	7
Formulation			
Epoxy resin, ^a pbw	100	100	100
Phenol/CH ₂ O/amine condensates, pbw			
Molar ratio: 1/1/1	54	—	—
1/2/2	—	43	—
1/3/3	—	—	43
Brookfield Viscosity, cps, 25°C	4000	4500	7000
Gel time, min (200 g mass)	19.2	43.3	59.7
Peak exothermic temperature, °C	201.8	210.0	202.5
Time to peak temp., min	24.7	55.0	70.5
Properties of cured 1/8-in casting^b			
Rheometric impact, total energy, in-Ib	61	38	33
Tensile strength, psi	8650	8400	8000
Tensile modulus, psi	471,000	392,000	358,500
Elongation at break %	8.5	6.8	11.2
Flexural strength, psi	14,500	14,400	13,000
Flexural modulus, psi	445,500	382,000	386,000
HDT, C., 264 psi/66 psi	50/52	65/73	67/72
Shore D hardness, 0–10 s	80–77	80–77	79–76
Compression strength at yield, psi	9600	10,200	9800
at failure, psi	48,600	36,800	37,500
% Compression at peak	69.6	60.3	60.0
% Weight gain, 24 h water boil	2.6	3.6	3.9
3 h acetone boil	7.4	2.7	2.6
Adhesive properties^c			
Tensile shear strength, psi	3600	4000	4100
T-peel strength, pli	4.3	4.2	4.3

^a Diglycidyl ether of bisphenol A, epoxy equivalent weight 185–192.

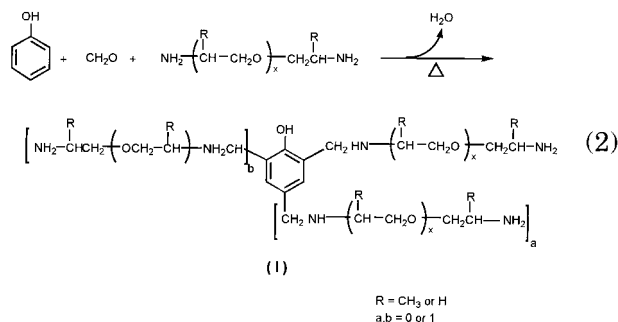
^b Cured 2 h 80°C, then 3 h 150°C.

^c Cured 1 h 150°C.

tionalities stoichiometrically through formaldehyde to *o*- and *p*-positions of phenols.

A series of Mannich condensates were prepared from bis(aminoethyl)ether, triethyleneglycol diamine, tetraethyleneglycol diamine, and polyoxypropylene diamines and triamine (i.e., Jeffamine[®] D-230/D-400 and T-403), according to eq. (2). The reaction, proceeding with the conversion of primary amines into secondary amine, can be easily monitored by amine titration.

The starting polyoxyalkylene polyamines (IIa–IIb in Fig. 1), available commercially via reductive amination²¹ of the corresponding polyoxyalkylene polyols in the presence of ammonia, hydrogen, and a heterogeneous Ni catalyst, can be classified into polyoxyethylene amines and polyoxypropylene amines.



The terminating oxyethylene and oxypropylene amine structures are derived from ethylene oxide and propylene oxide alkoxylation, respectively, in polyol preparation. Polyetheramines containing oxyethylene amines have higher curing activities than that of oxypropylene amines.¹⁹ Certain mo-

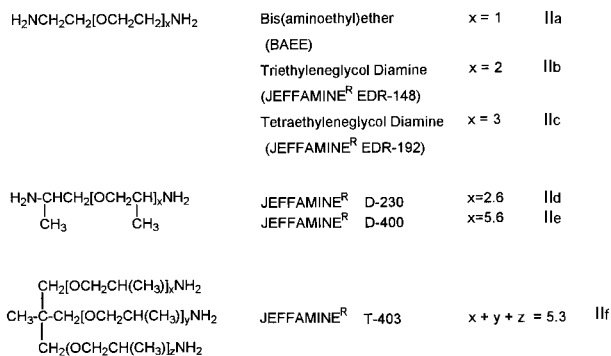


Figure 1 Structures of polyoxyalkylene polyamines.

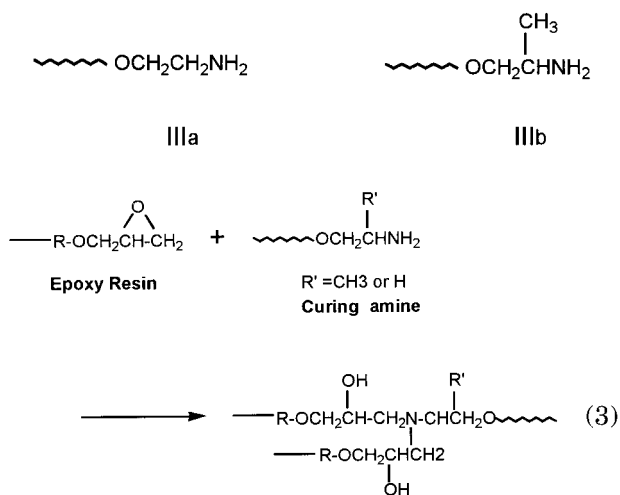
lecular weights of poly(oxypropylene) amines at approximately 200–500 such as Jeffamine[™] D-230, D-400, and T-403 are most suitable for epoxy curing agents. The polyoxypropylene amines, commercially available only at low molecular weights such as bis(aminoethyl) ether, triethyleneglycol diamine, and tetraethyleneglycol diamine, are generally not considered as desired epoxy curing agents, because of their too high crosslinking and oily surface in cured materials. With various substrate ratios, these polyoxyalkylene amines were allowed to react with phenol and formaldehyde to generate Mannich condensates, which are more suitable for epoxy curing. The variation of Mannich structures is depicted in eq. (2). The structure represents phenol-containing polyoxyalkylene polyamines with various molecular weights and multiple amine functionalities. Physically, these products were viscous liquid with analyzed amine contents consistent with calculated values. However, it was observed that certain Mannich adducts such as phenol/formaldehyde bis(aminoethyl) ether (BAEE) or triethyleneglycol diamine at 1 : 3 : 3 could not be prepared due to the crosslinking gel formation through the multiple reactive sites of phenol. A gel product was also formed when 4 mol of phenol and 4 mol of formaldehyde were reacted with 1 mol of triethyleneglycol diamine.

Relative Reactivity

At 1 : 1 : 1 molar ratio of phenol, formaldehyde, and various polyoxypropylene or polyoxyethylene amines, the condensates were made and tested for their relative reactivities towards epoxy curing agents [eq. (3)]. Summarized in Table I, these amines were evaluated by comparing the surface

drying time and gel time of the coating materials. It was found that the reactivities decreased in the following order: BAEE > Jeffamine[™] EDR-148 > Jeffamine[™] EDR-192 > Jeffamine[™] D-230, Jeffamine[™] T-403 > Jeffamine[™] D-400.

The trend can be best accounted for by the molecular weight, steric hindrance, and multiplicity of amines in the structures. When the molecular weight increased, the amine reactivity decreased from BAEE (molecular weight = 104) to Jeffamine[™] EDR-148 (148) to Jeffamine[™] EDR-192 (192), as well as from Jeffamine[™] D-230 (average molecular weight at 230) to Jeffamine[™] D-400 (400). With respect to the different types of polyoxyalkylene amines, polyoxyethylene amines such as BAEE, Jeffamine[™] EDR-148, and EDR-192 amines were found to have considerably higher reactivities than polyoxypropylene amines. The difference of the amine reactivities is attributed to the steric hindrance on the amine vicinity (structure IIIa vs. IIIb). The amine connected with the secondary carbon of polyoxypropylene backbone has low reactivity due to the steric hindrance. In contrast, primary amines positioned at primary carbon of poly(oxyethylene) backbone are rendered less steric hindrance structures and consequently higher reactivity. Significant increase in reactivity from Jeffamine[™] D-400 to T-403 is due to the structural change from two to three amine groups within similar molecular weight ranges.



Mannich Amine Structures and Epoxy Curing Properties

Selected Mannich amines including bis(aminoethyl) ether, triethyleneglycol diamine, and tetra-

ethyleneglycol diamine condensates were allowed to cure with glycidyl ether of Bisphenol A [eq. (3)]. The curing process and physical properties of these materials are summarized in Tables II, III, and IV. Some important features regarding the relationship between the amine structures and epoxy physical properties are noted below:

1. The preparation using higher molar ratio of amine to phenol gave rise to the Mannich condensates with higher molecular weight and higher viscosity. When cured with epoxy resin, the gel time was prolonged, in comparing sets of example 1 to 2 (Table II), 3 to 4 (Table III), and 5 to 6 to 7 (Table IV). Another trend was observed for Mannich condensates prepared from BAEE to triethyleneglycol diamine to tetraethyleneglycol diamine. At the same molar ratio of phenol to amine, the viscosity of condensates were lower and the gel time longer when using a higher molecular weight of amine. This may be due to their decreasing crosslinking density in relation to the presence of phenol structure, which could contribute to the shorter gel time during curing.
2. The cured epoxy materials have improved impact strength with increasing molecular weight of polyoxyethylene amine from example 1 (26 in-lb) to 3 (40 in-lb) to 5 (61 in-lb), and also from example 2 (18 in-lb) to 4 (22 in-lb) to 6 (38 in-lb). This trend represents the result of relatively lower crosslinking density with increasing molecular weight of Mannich amines. Similarly, when the molar ratio of phenol/formaldehyde/amine in Mannich condensates vary from 1 : 1 : 1 to 1 : 2 : 2 to 1 : 3 : 3, the resulting materials have lower impact strength, by comparing example 5 (61 in-lb), 6 (38 in-lb), and 7 (33 in-lb).
3. In contrast to the impact strength, the heat distortion temperature (HDT) slightly decreases with the increasing molecular weight of the Mannich amines, or lowering crosslinking density. However, the trend is not as obvious as in impact strength by comparing example 1 (BAEE) to example 3 (triethyleneglycol diamine) to example 5 (tetraethyleneglycol diamine).
4. Other physical properties, including tensile, flexural, compression strength, and

hardness, have no obvious trends in relating to the variation of polyoxyethylene amines. However, the Mannich amines derived from triethyleneglycol diamine seem to have an overall balance of properties, which are better than those of BAEE and tetraethyleneglycol diamine derivatives. This may be attributed to the proper structural balance of phenol (rigid) and triethyleneglycol diamine (flexible and crosslinking) in the Mannich amines as epoxy curing agents.

5. The higher molecular weight of poly(oxyethylene)diamine derivatives produced materials with better adhesive properties, in terms of tensile shear and T-peel strength.

This is evidenced by comparing the results obtained from tetraethyleneglycol diamine derivatives with that of BAEE and triethyleneglycol diamine. The cured epoxy with phenol/formaldehyde/tetraethyleneglycol diamine (1 : 3 : 3 molar ratio) condensate have the best adhesive property of tensile shear (4100 psi) and T-peel strength (4.3 pli) among Mannich amines studied.

CONCLUSION

Mannich condensates of polyoxyalkylene amines including polyoxypropylene and polyoxyethylene diamines with molecular weight range of 104 to 400 were prepared. This reaction can be generalized, except certain Mannich products. At 1 : 3 : 3 molar ratio, phenol/formaldehyde/bis(aminoethyl)ether (BAEE) or triethyleneglycol diamine adducts could not be prepared successfully due to the crosslinking gel formation through the multiple reactive sites of phenol. The reactivity of polyoxyethylene diamine-derived Mannich condensates is significantly higher than that of polyoxypropylene derivatives when cured with the glycidyl ether of Bisphenol A. The curing reactivity, represented by gel time and drying time, is correlated well with amine structures according to the following order: BAEE > Jeffamine™ > EDR-148 > Jeffamine™ EDR-192 > Jeffamine™ D-230 ≅ Jeffamine™ T-403 > Jeffamine™ D-400.

This trend can be best explained by the molecular size, steric hindrance, and amine multiplicity of the Mannich structures. The properties of epoxy materials such as impact, tensile, hardness, and flexural strength were measured and found

to be correlated with the molecular weight and the crosslinking density. Triethyleneglycol diamine-derived Mannich amines appears to have better overall balance of physical properties than those of BAEE and tetraethyleneglycol diamine. By comparison, the Mannich amine of tetraethyleneglycol diamine at 3 : 1 molar ratio to phenol is the most favorable structure with respect to the adhesion properties.

The original data are patented in G. P. Speranza, H. G. Waddill, and J. J. Lin, U.S. Pat. 5,120,817 (1992) to Texaco Chemical Co.

REFERENCES

1. F. F. Blicke, in *Organic Reactions*, vol. 1, J. Wiley and Sons, New York, 1942, p. 303.
2. M. Tramontini, L. Angiolini, and N. Ghedini, *Polymer*, **29**, 771 (1988).
3. D. A. Leigh, P. Linnae, and G. Jackson, *Tetrahedron Lett.*, **34/35**, 5639 (1993).
4. B. B. Thompson, *J. Pharmacol. Sci.*, **57**, 715 (1968).
5. M. Tramontini, *Synthesis*, 703 (1973).
6. J. H. Hodgkin, *J. Polym. Sci., Part A: Polym. Chem.*, **24**, 3117 (1986).
7. G. B. Butler and S. H. Hong, *J. Macromol. Sci.-Chem.*, **A24**, 919 (1987).
8. L. Angiolini, N. Ghedini, and M. Tramontini, *Polym. Commun.*, **26**, 218 (1985).
9. S. H. Brown, S. Rafael, and R. E. Crocker, U.S. Pat. 3,868,329 (1975) to Chevron Research Company.
10. P. V. Roling, J. H. Y. Niu, and D. K. Reid, U.S. Pat. 4,810,354 (1989) to Betz Laboratories, Inc.
11. J. T. Loper, U.S. Pat. 5,387,266 (1995) to Ethyl Corporation.
12. D. Jamois, M. Tessier, and E. Marechal, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 1941 (1993).
13. M. E. Brennan and G. P. Speranza, U.S. Pat. 4,487,852 (1984) and 4,484,195 (1984).
14. H. Suzuki, A. Matsui, and T. Inoue, U.S. Pat. 3,950,451 (1976) to Asahi Denka Kogyo K. K.
15. W. Becker, U.S. Pat. 3,734,965 (1973) to Reichhold-Albert-Chemie.
16. C. A. May, *Epoxy Resins, Chemistry and Technology*, Marcel Dekker, Inc., New York, 1988.
17. M. M. Baffa and C. H. Bull, U.S. Pat. 4,659,779 (1987) to Ciba-Geigy Corporation.
18. R. A. Grigsby, Jr. and G. P. Speranza, U.S. Pat. 4,714,750 (1987) to Texaco Inc.
19. J. J. Lin, G. P. Speranza, and H. G. Waddill, *J. Polym. Res.*, **3**, 2, 97 (1996).
20. P. J. Chenier, *Survey of Industrial Chemistry*, 2nd ed., VCH Publishers, New York, 1992, p. 290.
21. P. H. Moss, U.S. Pat. 3,152,998 (1964) to Jefferson Chemical Co.