Polymer Bulletin 36, 295-302 (1996)

Polymer Bulletin

© Springer-Verlag 1996

Preparation of metal-aromatic diamine complexes and their influence on the cure of a commercial epoxy resin

Ian Hamerton [1,*], Brendan J. Howlin [1], John R. Jones [1], Shuyuan Liu [1], John M. Barton [2]

[1] Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, UK
[2] Structural Materials Centre, Non-Metallics, Defence Research Agency,
Farnborough, Hampshire, GU14 6TD, UK

Received: 28 August 1995/Revised version: 9 October 1995/Accepted: 1 November 1995

Summary

The preparation of metal-aromatic diamine complexes is reported along with their characterisation by infrared spectroscopy. Dynamic viscometry (gel-point determination) was used to assess the reactivity of some of the metal-diamine complexes with a commercial epoxy resin. Significant differences were observed in the viscosity profiles for formulations with different metal contents. These related to the reactivities of the diamines which are themselves a function of metal content.

Introduction

Previous work has demonstrated that metal ions can be used to induce latent behaviour in imidazoles used for curing epoxy resins (1-3). Amines (both aliphatic and aromatic) are more commonly used as curing agents and also have the potential to complex with metal ions. The introduction of metal ions may also affect the conductivity and dielectric relaxation of the cured polymer and this in turn depends upon the concentration and mobility of the ions in the resin. It has also been claimed that the incorporation of metal ions in resin matrices has improved the thermal stability and resistance to oxidation (4,5). There are at least two methods whereby metal ions can be introduced into an epoxy system. The first is through the use of colloidal particles, but difficulties associated with this technique are poor reproducibility and sedimentation. The second method is to use metal chelates and the metal ion of choice is copper which is known to be a good inhibitor of thermal oxidation (5). Complexes of aromatic amines are preferable to aliphatic amines because the cured products display improved thermal stability. The steric arrangement of the amino groups is important: *ortho* substitution favouring the formation of five-membered chelate rings, whereas *meta* and *para* substitution favour the formation of linear structures. It is possible, therefore, by modifying the structure of the curing agent to alter their reactivity with respect to epoxides. This control of the rate of cure will allow the use of widely differing curing temperatures. In addition, mixed ligand chelates are possible and these can be used to increase solubility or lower the melting point.

Experimental

Preparation of complexes

Copper(II) chloride complexes of *ortho*-phenylene diamine (OPD), *para*-phenylene diamine (PPD), diaminodiphenyl methane (DDM) and diaminodiphenyl sulphone (DDS) were prepared by refluxing the reagents (the amine and metal salt in a molar ratio a[amine]: m[metal]; a = 1-6, m = 1) in absolute ethanol (20-30 minutes). Products were isolated by filtration or by evaporating the solvent to give crystalline (or

---

* Corresponding author

microcrystalline powder) materials. Characterisation was carried out by monitoring the N-H stretching (3340 cm^{-1}) and deformation bands (1280 cm^{-1}) in the infra-red (IR) before and after association with copper.

Materials

The commercial epoxy monomer, 'EPON 825' (*ex* Shell), is a high purity grade of bisphenol A diglycidyl ether (BADGE). The structure is nominally represented by (*1*) below and referred to in Scheme 1). OPD, PPD, DDM, DDS and $CuCl_2$ were obtained from Aldrich Chemical Company. Purities were determined using ^1H n.m.r. (with the exception of $CuCl_2$ - for which elemental analysis was used) and the compounds used as received.

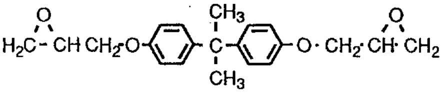


Figure 1. Commercial epoxy monomer EPON 825 (BADGE) (*1*).

Equipment

Measurements of dynamic (rotational) viscosity were made on the commercial epoxy/curing agent mixtures using a Brookfield RVTD113 viscometer (using an RV7 spindle) operating at a range of temperatures and at a fixed shear rate of 64 Hz. IR measurements were made on a Perkin-Elmer 1750 FT-IR spectrometer interfaced with a Perkin-Elmer 7300 computer; the samples were presented as KBr disks.

Results and discussion

Preparation

Two methods were investigated to prepare the copper-aromatic diamine complexes. The preparation of similar complexes has been described (4) by mixing both the metal salt and amine in a molten state. It was difficult to obtain pure complexes by this route and the high melting points of some of the reagents (*e.g.*, DDS, mp 175-177°C) led to some undesirable side reactions including the decomposition of thermally unstable compounds such as copper(II) acetate, oxidation of the amino group to the nitro derivative and evaporation of volatile materials such as OPD (making it hard to maintain the stoichiometric balance). The result of these difficulties was to produce a multi-component mixture containing many impurities and low yields of the desired metal-amine complex. Furthermore, the resulting products were often infusible, making it hard to dissolve in either solvents or the epoxy monomer. This poor solubility had the added disadvantage of making isolation and analysis of the complexes difficult.

An alternative method which proved successful was to gently reflux the reagents together in absolute ethanol until complexation had occurred (as evidenced by IR measurements). Once the solvent had been removed no further attempt was made to remove the 'free' (unassociated) amine species. The preparation of a low metal content curing agent such as $Cu(OPD)_2Cl_2$ avoids the incorporation of a high metal content which might be undesirable in some applications. Incorporation of large quantities of this complex tends to produce an 'inorganic' polymer by introducing more dative covalent bonds at the expense of covalent bonds, the latter having higher thermal stability and yielding products with better mechanical properties. Unfortunately, it was not possible to produce a preparative route to yield a single complex in high yield - the complex formed from a 2:1 mole ratio of OPD and $CuCl_2$ displayed free amino groups indicating that there is a mixture of complexes present. However, for our experiments to determine the effect of complexation it was sufficient to have an accurate knowledge of the metal content. Once mixed with the epoxy monomer and at the cure temperature, the mixture contains largely dissociated amine species.

Characterization

A series of spectral analyses was carried out on the diamines (OPD, PPD, DDM and DDS) and metal-diamine complexes [$Cu(OPD)Cl_2$, $Cu(OPD)_2Cl_2$, $Cu(PPD)Cl_2$,

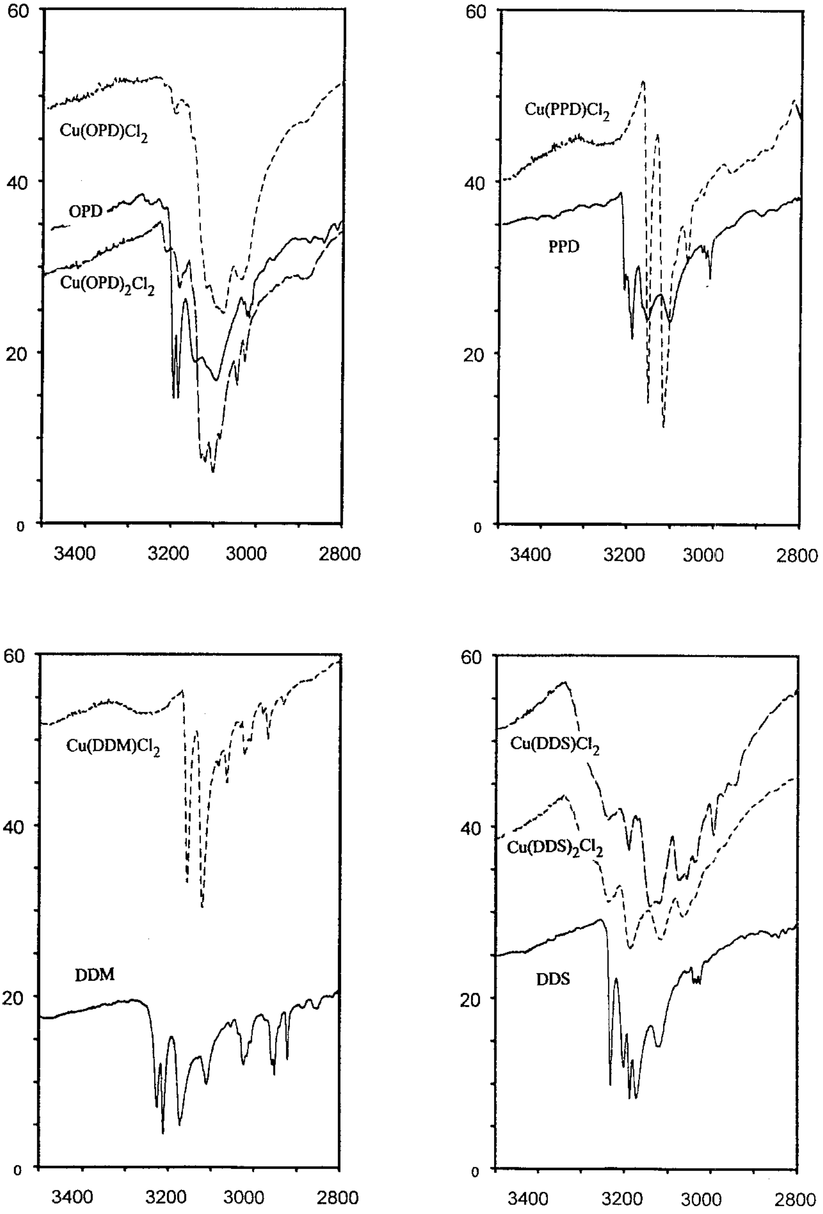


Figure 2.Infra-red spectra (% Transmission *versus* wavenumber, cm^{-1}) of diamines and their copper(II) complexes

$Cu(PPD)_2Cl_2$, $Cu(DDM)Cl_2$, $Cu(DDM)Cl_2$, $Cu(DDS)Cl_2$ and $Cu(DDS)_2Cl_2$] (Fig. 2). In most cases, when the diamine and $CuCl_2$ were in stoichiometric balance then the 1:1 complexes were the most favourable and stable products regardless of the starting materials used. No 'free' amine bands were observed indicating the formation of a linear complex structure through intermolecular (binuclear) bridge bonds. The structure of OPD with adjacent binding sites should favour the formation of a chelate with copper (which offers the benefit of better solubility in epoxy) while PPD produces linear complex structures (see Scheme 2) which are of lower solubility when formulating the curing agent and epoxy monomer. In cases where the diamine was used in excess over the $CuCl_2$ then free amine groups were observed indicating that some diamines are only partially associated with the metal or not at all. The increase in the number of ligands bonding to the metal leads to a decrease in the stability of the resulting ligand bonds.

Formulation with epoxy monomer (1)

Imidazole curing agents are often applied in small quantities (*ca.* 5-7 weight %) in epoxy resins (1-3, 6), whereas aromatic amines are normally present in stoichiometric amounts. Hence, the incorporation of a 1:1 metal diamine complex (*e.g.*, $Cu(OPD)^{2+}$) will introduce a high metal ion content. The reactivity and degree of conversion is likely to be affected markedly by this. Additionally, there is a greater chance of the metal ion coordinating with (and being incorporated into) the final network. This may have an effect on the final network properties.

Reaction of OPD and PPD complexes with epoxy (*1*)

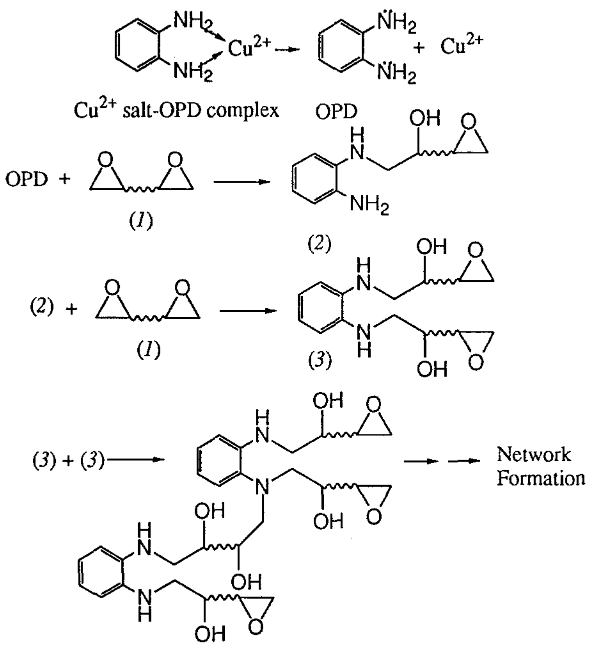
In the reaction between OPD and (*1*) the amine groups react with the epoxide group to form a 1:1 adduct (Scheme 1). The reaction of a second amino group with epoxy (*1*) will form a 1:2 adduct. The reaction of 1° and 2° amine groups with an epoxide group on another adduct will produce a branched structure and finally the reaction of a second 2° amino group with branched products will lead to a crosslinked network. Whilst this is the actual reaction mechanism the kinetics of the reaction are complicated by autocatalysis which is caused by the hydroxyl groups produced and any hydroxyl containing impurities in the reaction mixture. The analogous reaction between PPD and (*1*) is shown in Scheme 2. While the actual reaction steps in the mechanism are identical to that of OPD, the effect is to produce a more linear, less branched network during the formative steps with more oligomers of similar molecular weight present at gel-point.

Dynamic viscometry studies

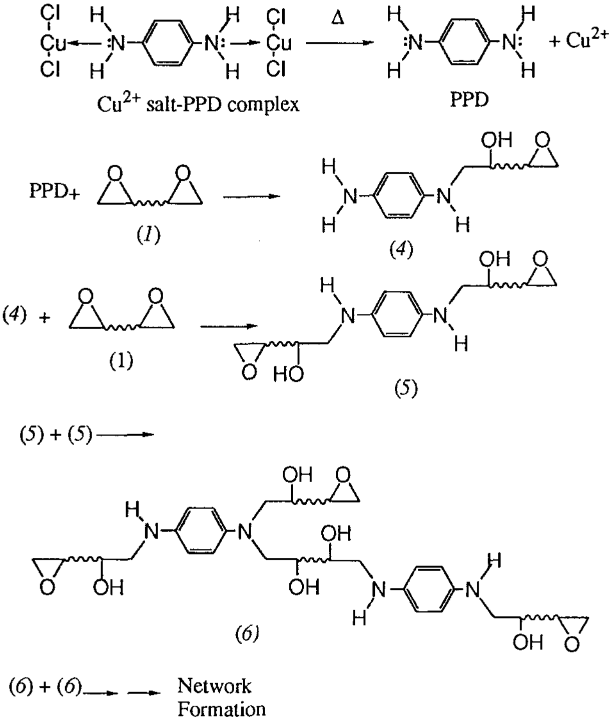
Dynamic measurements of viscosity were made (from measurements of the gelation as a function of time and temperature) during the cure of the epoxy-complex formulations to gain an understanding of the relative reactivity of the systems and of the mechanism of network formation (by applying the concepts of self-similar fractal growth and scaling theory to the viscosity data) (7-9).

Dynamic viscometry of OPD and PPD complexes with epoxy (*1*)

Three formulations: OPD, $Cu(OPD)Cl_2$ and $Cu(OPD)_2Cl_2$ with epoxy (*1*) were monitored over time at 100°C. Fig. 3 shows the viscosity *versus* time plot for these three formulations. Significant differences were observed in the viscosity profiles for formulations with different metal contents. The reactivity of the amines decreases with increasing metal content, the initial network (as shown by t_{gel}) is formed for curing agents OPD, $Cu(OPD)_2Cl_2$ and $Cu(OPD)Cl_2$ at 36, 37 and 53 minutes respectively. These results indicate that although the complex could be dissociated at this curing temperature, the interaction between NH_2 and Cu^{2+} has hindered the reaction between the NH_2 and epoxide groups.



Scheme 1. Proposed reaction of epoxy (*1*) with OPD complex curing agents



Scheme 2. Proposed reaction of epoxy (*1*) with PPD complex curing agents

Table 1. Viscosity behaviour for the cure of OPD/epoxy systems at 100°C

	OPD	$Cu(OPD)_2Cl_2$	$Cu(OPD)Cl_2$
t_{gel} (min)	35.5	37	53.5
Δt_{gel} (min)	< 4	14	10

t_{gel}	time at which viscosity tends to infinity
Δt_{gel}	time taken for the onset of gelation to full gelation

From Δt_{gel} values (Table 1) it can be seen that the OPD formulation exhibits a very rapid increase in viscosity at the gel point, suggesting that the cure follows the mechanism shown in Scheme 1. The 1:1 complex system behaves in a similar fashion, although gelation is delayed and the increase in viscosity is not as pronounced as the OPD system (the large amount of metal salt present may resist further crosslinking by either coordination or steric hindrance). Although the reactivity does not decrease dramatically with the reduction in metal content, a marked difference in viscosity profile is obtained for the 1:2 system which displays an earlier onset, but a slower increase in viscosity (indicating a less even growth in molecular weight). Because the amino groups cannot fully associate or interact with the metal ion, there are many free NH_2 groups in the system leading to a range of amino groups of differing reactivities. As a result the reaction cannot proceed evenly and a number of oligomeric species (of different molecular weights) is present at the gel-point.

Four formulations: PPD, $Cu(PPD)_2Cl_4$, $Cu(PPD)_4Cl_2$ and $Cu(PPD)_6$ with epoxy (*1*) were monitored over time at 80°C. Fig. 4 shows the viscosity *versus* time plot for these four formulations. The poor solubility and high melting point (143-145°C) pose particular problems with PPD making it difficult to disperse the curing agent in the resin. The PPD has to be granulated finely before mixing with the epoxy (*1*) and stirred frequently during the cure to avoid aggregation and precipitation. In contrast the complexes of PPD form fine particles making the handling easier. The dynamic viscometry data are shown in Fig. 4 and presented in Table 2.

Table 2. Viscosity behaviour for the cure of PPD/epoxy systems at 80°C

	PPD	$Cu(PPD)_6$	$Cu(PPD)_4Cl_2$	$Cu(PPD)_2Cl_4$
t_{gel} (min)	20	18	21	> 72
Δt_{gel} (min)	< 1	2	3	> 30

t_{gel}	time at which viscosity tends to infinity
Δt_{gel}	time taken for the onset of gelation to full gelation

The results are similar to those for the OPD systems in that an increase in the metal content of the PPD system results in a decrease in reactivity of the formulated epoxy mixture (Table 2). The exception is the pure PPD system which is slower to reach gelation than the 6:1 complex, but this may be a result of the particle size which is bigger than the finely powdered complexes and the poor solubility (making the effective concentration lower than expected). From Table 2 and Fig. 4 it can be seen that gelation of the PPD system can be reached in a shorter time scale (20 minutes) and at lower temperature (80°C) than the OPD system (35.5 minutes at 100°C). The greater reactivity of PPD may be attributable to the lower steric hindrance in the amine/epoxy reaction. However, at the same temperature both 1:1 and 1:2 copper/PPD complex systems are relatively unreactive (each take more than 4 hours to reach gel point). This is probably because most of the amino groups are coordinated with the metal in compositions containing such a high metal content and the coordination of 1:1 and 1:2 complexes are inherently strong through linear or network bridge bonds (which are still stable at this temperature). At a cure temperature of 100°C, the reactivity of all PPD complexes (including 1:1 and 1:2) increases dramatically indicating that the ligand bonds are broken at this temperature. The PPD formulations show viscosity profiles

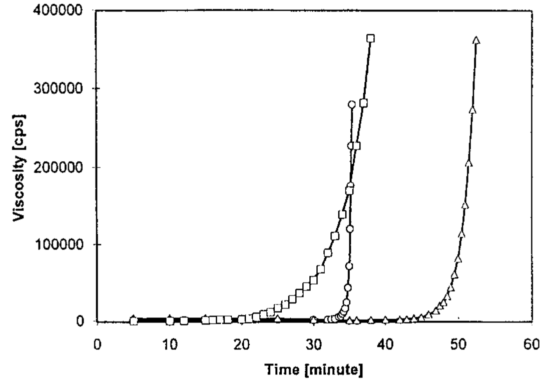


Figure 3. Dynamic viscosity of BADGE/OPD (o), BADGE/Cu(OPD)Cl_2 (△) and BADGE/Cu$(OPD)_2CL_2$ (□) at 100°C

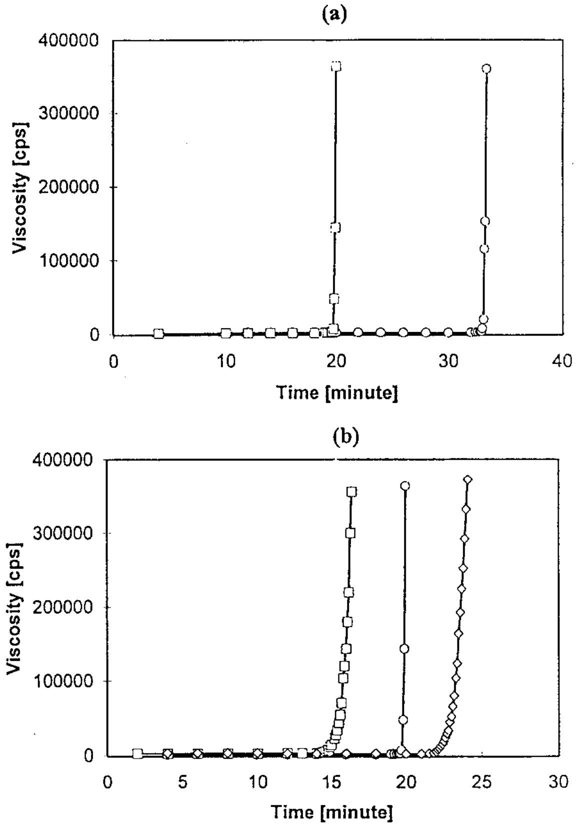


Figure 4. (a) Dynamic viscosity of BADGE/PPD at 75 (o) and 80°C (□)

(b) Dynamic viscosity of BADGE/PPD complex systems- (o) PPD, (□) $Cu(PPD)_6^{2+}$, (◇) $Cu(PPD)_4^{2+}$

which are typical of percolation network formation mechanism (albeit perhaps an extreme example) at a range of temperatures (Fig. 4). The viscosity shows a considerable increase at gel point indicating that the cure process undergoes an orderly progress as shown in Scheme 2. 1:4 and 1:6 systems also show the percolation style of network formation but again as in the copper OPD complex systems the network formation process is retarded by the presence of metal ions in the system.

Conclusions

Dynamic viscometry was used to assess the reactivity (by sol-gel transition determination) of a series of metal-diamine complexes with a commercial epoxy resin (EPON 825). Complexes of aromatic diamines including OPD, PPD, DDM and DDS were studied enabling a study of the effect of the steric arrangement of the amino groups upon both complex geometry (*ortho* substitution favouring the formation of five-membered chelate rings and *meta* and *para* substitution favouring the formation of linear structures) and also on the nature of the network formation. The OPD/epoxy and PPD/epoxy formulations and their corresponding metal complexes were examined for their rheological behaviour during cure. Significant differences were observed in the viscosity profiles for formulations with different metal contents as the reactivity of the diamines decreases with increasing metal content. The polymer networks containing OPD formulations appeared to undergo a mechanism involving more branched oligomers, while the analogous PPD formulations appeared to conform to a more linear, even chain extension prior to crosslinking. It is possible to modify the structure of an amine curing agent to alter its reactivity with respect to epoxides. This control of the rate of cure will allow the use of widely differing curing temperatures. In addition, mixed ligand chelates are possible and these can be used to increase solubility or lower the melting point. Adjusting the metal content of the polymer matrix offers the opportunity to 'fine tune' many properties such as dielectric behaviour, water and chemical resistance, thermal and mechanical characteristics. This general approach may have even greater potential to provide 'latent' curing properties to 'fast' cure systems such as aliphatic diamines (these molecules can readily form stable multidentate complexes with transition metals) and work continues to explore this exciting area of materials chemistry.

Acknowledgements

This work was generously supported by the Structural Materials Centre, Defence Research Agency, Farnborough.

References

1. Barton JM (1984) GB Patent 2,135,316 B
2. Dowbenko R, Anderson CC and Chang WH (1971) *Ind. Eng. Chem. Prod Res. Develop.* 10: 344
3. (a) Barton JM, Buist GJ, Hamerton I, Howlin BJ, Jones JR and Liu S (1994) *J Mater Chem* 4: 379; (b) Buist GJ, Hamerton I, Howlin BJ, Jones JR, Liu S and Barton JM, (1994) *J Mater Chem* 4: 1793; (c) Barton JM, Buist GJ, Hamerton I, Howlin BJ, Jones JR and Liu S (1994) *Polym. Bull.* 33: 215; (d) Barton JM, Hamerton I, Howlin BJ, Jones JR and Liu S (1994) *Polym. Bull.* 33: 347; (e) Hamerton I, Howlin BJ, Jones JR, Liu S and Barton JM (1995) Studies of cure schedule and final property relationships of commercial epoxy resins using modified imidazole curing agents, submitted
4. Kurnoshkin AV (1992) *Ind. Eng. Chem. Res.* 31: 524
5. Kurnoshkin AV (1991) *Polym.-Plast. Technol. Eng.* 30: 737
6. Ashcroft WR Curing Agents for epoxy resins Chapter 2 in *"Chemistry and Technology of Epoxy Resins"*, ed. B Ellis, Blackie Academic and Professional, Glasgow (1993) 58-59.
7. Adolf D, Martin JE and Wilcoxon JP (1990) *Macromolecules* 23: 527
8. Mijovic J, Kenny JM and Nicolais L (1993) *Polymer* 34: 207