

Epoxy/Anhydride Networks Modified by Epoxy/Anhydride Oligomers Containing SiOH Groups

ADRIANA N. MAURI, CARMEN C. RICCARDI, ROBERTO J. J. WILLIAMS

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, (7600) Mar del Plata, Argentina

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ABSTRACT: Epoxy/anhydride oligomers containing variable amounts of trialkoxysilane groups were synthesized from phenyl glycidyl ether (PGE), 3-glycidoxypropyl trimethoxysilane (GPMS), and methyl tetrahydrophthalic anhydride (MTHPA), using benzyldimethylamine (BDMA) as an initiator. They were hydrolyzed and partially condensed using diluted formic as a catalyst, with the last step carried out in a solution of diglycidyl ether of bisphenol A (DGEBA). By curing with a stoichiometric amount of MTHPA, in the presence of BDMA, plasticized epoxy/anhydride networks were obtained without any evidence of phase separation. These materials showed a better abrasion resistance than that of the neat matrix. The presence of free SiOH groups can be used to improve the adhesion to glass surfaces. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1365–1370, 2000

Key words: epoxy/anhydride networks; SiOH-modified epoxy/anhydride oligomers; plasticized epoxies; abrasion resistance

INTRODUCTION

In the search of epoxy coatings with improved abrasion resistance and adhesion to glass surfaces, we investigated the effect of adding epoxy/anhydride oligomers functionalized with free SiOH groups. The following route was used to generate the SiOH-functionalized additives: First, epoxy/anhydride oligomers containing trialkoxysilane groups were synthesized. They were then hydrolyzed and partially condensed using diluted formic as a catalyst, with the last step carried out in a solution of diglycidyl ether of bisphenol A (DGEBA). By curing with a stoichiometric amount of an anhydride and a tertiary amine as an initiator, a plasticized polymer net-

work was obtained without any evidence of phase separation. Several properties of the modified networks were determined and compared with those of the neat epoxy matrix.

EXPERIMENTAL

Materials

The structures of the different chemical reagents are shown in Figure 1. The selected monoepoxides were phenyl glycidyl ether (PGE, Aldrich, Milwaukee, WI) and 3-glycidoxypropyl trimethoxysilane (GPMS, Sigma, St. Louis, MO). The diepoxide was DGEBA (MY 790, Ciba-Geigy, with an average n value equal to 0.03). It was carefully dehydrated before use. The epoxides were polymerized with methyl tetrahydrophthalic anhydride (MTHPA, HY 918, Ciba-Geigy), using benzyldimethylamine (BDMA, Sigma), as an initiator, in an amount of 0.04 mol per mol of epoxy groups.

Correspondence to: R. J. J. Williams.
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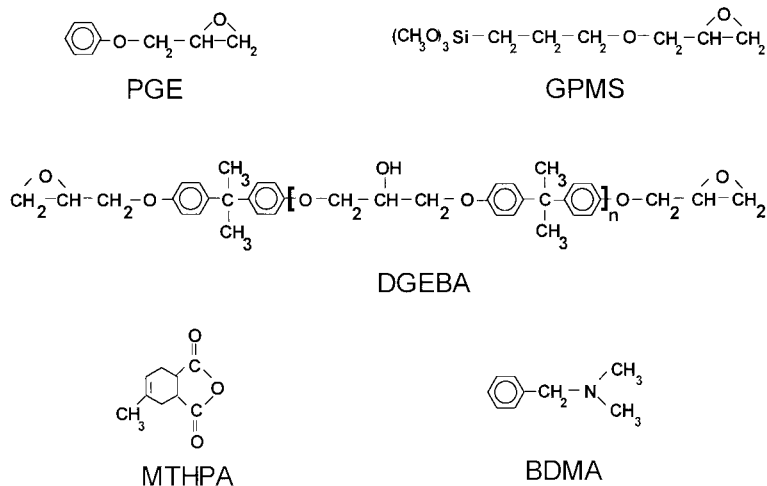


Figure 1 Chemical reagents.

Characterization

Molar-mass distributions were determined by size-exclusion chromatography (SEC), with a Waters 510 GPC provided with ultraStyragel columns 100 ($\times 2$), 500, and 1000, using a refractive index detector. Tetrahydrofuran (THF), at 1 mL/min, was used as a carrier. Fourier-transformed infrared spectroscopy was used to follow the polymerization and the hydrolytic condensation (FTIR, Bruker IFS 25 on NaCl windows).

Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC, DuPont 990 TA, onset value at 10°C/min under N_2) or by thermal mechanical analysis (TMA, Mettler TA 3000, onset value at 10°C/min using both static and dynamic forces). DSC (Mettler TA 3000) was also used to obtain the heat of reaction of the epoxy/anhydride polymerization.

Minicylindrical compression-test specimens with a diameter $D = 4$ mm and $L/D = 1.5$ were machined and deformed under an uniaxial compression mode in a Shimadzu Autograph S55-C universal testing machine. The crosshead displacement was measured using an LVDT placed very close to the specimen. The elastic modulus and the compressive yield stress, σ_{yc} , were determined from the experimental curves.

The microhardness was measured using a Wilson Tukon 300 device with a Vickers indenter, applying a 5 kg force for 15 s. The abrasion resistance was determined with a dry sand/rubber wheel apparatus (ASTM G65, 91, Procedure D).

RESULTS AND DISCUSSION

Synthesis of Epoxy/Anhydride Oligomers Containing Trialkoxysilane Groups

The copolymerization of epoxides with cyclic anhydrides in the presence of tertiary amines proceeds through an anionic chainwise mechanism comprising initiation, propagation, and chain-transfer steps. Propagation involves the alternating addition of epoxy and anhydride groups to the growing chain. But as the alkoxide at a chain end reacts at a faster rate than does the carboxylate,^{1,2} the (almost) simultaneous addition of an epoxy-anhydride couple to the growing chain takes place. A chain-transfer step that regenerates the active species must be present to account for the experimental values of the gel conversion.³ Figure 2 shows a fragment of a linear chain formed in the PGE/GPMS/MTHPA reaction.

The PGE/MTHPA copolymerization in stoichiometric amounts was first analyzed. Figure 3

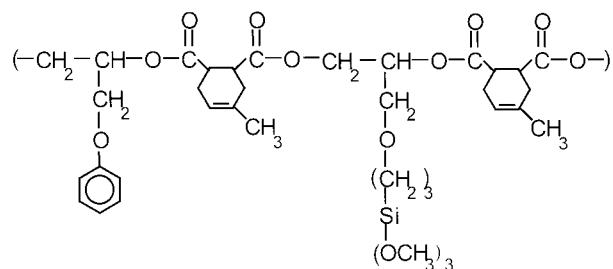


Figure 2 Fragment of a linear chain formed during the polymerization of PGE, GPMS, and MTHPA.

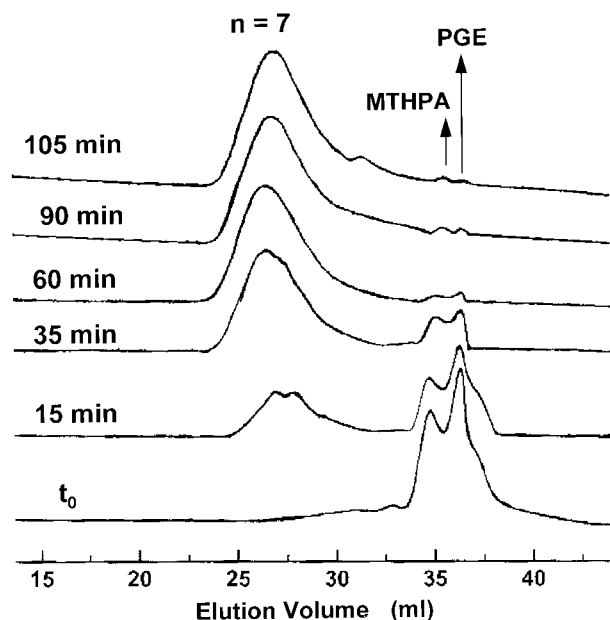


Figure 3 Evolution of SEC chromatograms for the PGE/MTHPA copolymerization initiated by BDMA at 100°C.

shows the evolution of SEC chromatograms during the reaction carried out in bulk at 100°C, using BDMA as an initiator. It is observed that the reaction reaches an almost complete conversion of both comonomers. The maximum of the SEC peak at full conversion corresponds to an oligomer containing 7 units of both comonomers [as a result from a calibration curve built up by using different condensation products of PGE and *N*-(β -aminoethyl)- γ -aminopropyltrimethoxysilane]. For a living polymerization and assuming that all of the added initiator becomes active, the average size of the oligomeric chains should be of 25 units of both comonomers (corresponding to the 0.04 mol of BDMA per mol of epoxy groups). The significantly lower value observed experimentally gives evidence of the presence of chain-transfer steps in the reaction mechanism.

The evolution of the individual conversions (x) of both comonomers was quantified by defining

$$x = 1 - h/h_0 \quad (1)$$

where h/h_0 is the ratio of the peak height at any time with respect to the initial value. Figure 4 shows that the evolution of both conversions is practically the same within experimental error. This is the expected result for an alternating copolymerization of epoxy and anhydride groups.

The terpolymerization of GPMS/PGE/MTHPA, initiated by BDMA, was then studied. The reaction was carried out at 70°C in tubes sealed under a vacuum to avoid the presence of water (it could initiate the hydrolytic condensation of the alkoxy-silane groups in parallel with the epoxy/anhydride reaction). Stoichiometric amounts of the total epoxy/anhydride groups were used. The molar ratio, $f_{\text{GPMS}} = \text{GPMS}/(\text{PGE} + \text{GPMS})$, was varied from 0 to 1. After 24 h at 70°C, a practically full conversion was attained as revealed by FTIR spectroscopy. As an example, Figure 5 shows the FTIR spectrum of the product synthesized with $f_{\text{GPMS}} = 1$. Bands at 1774 and 1830 cm^{-1} (anhydride groups) and at 912 cm^{-1} (epoxides) have disappeared, indicating complete conversion of both comonomers. No SiOH band was found in the 3200–3500 cm^{-1} range, a fact that proved that Si—OCH₃ groups were not hydrolyzed. This was also confirmed by the presence of bands at 2842 cm^{-1} (CH₃ symmetric stretch of the OCH₃ groups) and at 1088 and 817 cm^{-1} (asymmetric and symmetric stretch of Si—O—CH₃).⁴

Figure 6 shows the SEC chromatograms of the oligomers prepared with $f_{\text{GPMS}} = 0$ and 0.5. The presence of GPMS led to a broad distribution of oligomers, a fact that may result either from the increase in the rate of chain transfer or from the presence of intramolecular cyclization. Similar broad distributions were observed for different values of f_{GPMS} . Glass transition temperatures are shown in Figure 7. T_g decreases significantly with the proportion of GPMS in the initial formulation.

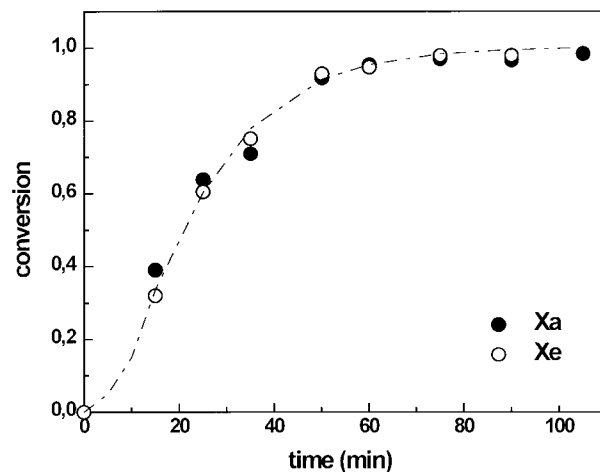


Figure 4 Conversion of epoxy (x_e) and anhydride (x_a) monomers during the PGE/MTHPA copolymerization initiated by BDMA at 100°C.

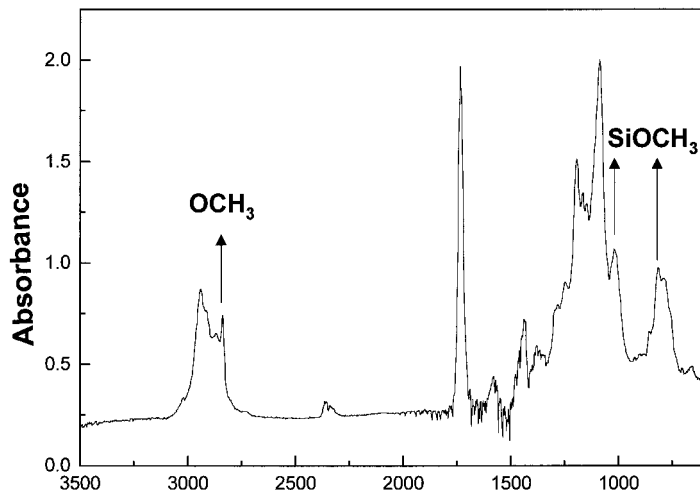


Figure 5 FTIR spectrum of the copolymer GPMS/MTHPA after 24 h at 70°C.

Obtention of SiOH-functionalized Epoxy/Anhydride Oligomers

Hydrolysis and partial condensation of the epoxy/anhydride oligomers containing trialkoxysilane groups was performed using both acid and basic catalysts. The following reactions take place:

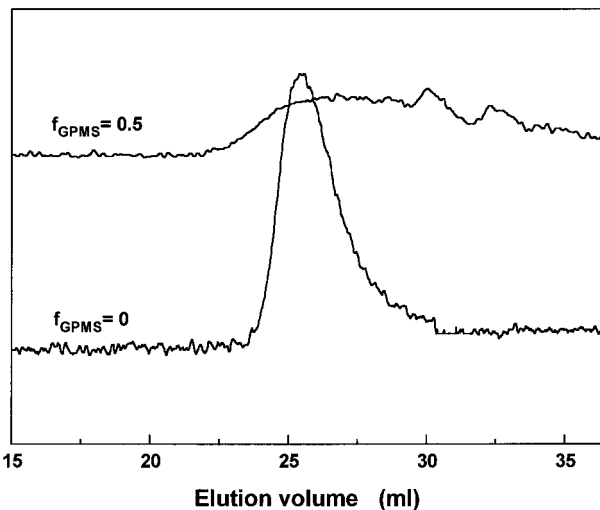
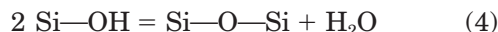


Figure 6 SEC chromatograms of the copolymer PGE/MTHPA ($f_{\text{GPMS}} = 0$) and the terpolymer PGE/GPMS/MTHPA ($f_{\text{GPMS}} = 0.5$) at complete conversion of the monomers.

A preliminary analysis of different reaction conditions was performed using the oligomer with $f_{\text{GPMS}} = 0.5$. Table I shows different catalysts and molar ratios used for the hydrolytic condensation in tetrahydrofuran (THF). The reaction was carried out using the following thermal cycle: 48 h at 40°C, a heating step up to 70°C where a vacuum was applied to eliminate volatiles, a heating period in steps up to 150°C, and a stage of 3 h at this temperature. The condensation product was a gel insoluble in THF. The progress of the hydrolytic condensation was followed by FTIR. Although the reaction rate depended on the selected catalyst, final IR spectra were indistinguishable (Fig. 8 shows one of these spectra).

According to the literature,⁴⁻⁷ broad bands at ≈ 1050 and 1100 cm^{-1} are assigned to Si-O-Si

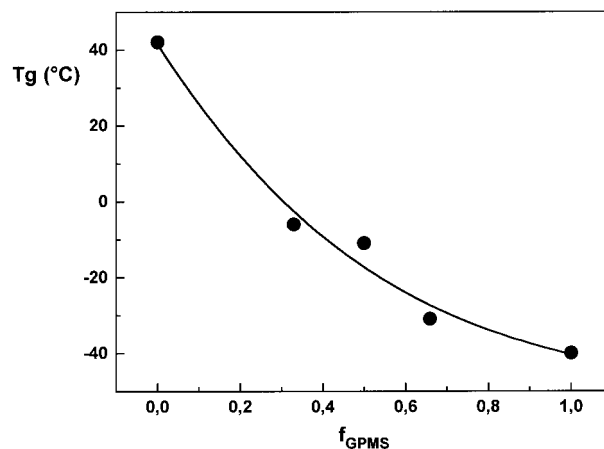


Figure 7 T_g of the PGE/GPMS/MTHPA terpolymers as a function of the proportion of GPMS in the initial formulation (f_{GPMS}).

Table I Catalysts and Molar Ratios Used for the Hydrolytic Condensation and T_g of the Resulting Products

| Catalyst | Molar Ratio | T_g (°C) |
|-----------|-------------------------|------------|
| ClH 2M | H ₂ O/Si = 3 | -14.5 |
| NaOH 1M | H ₂ O/Si = 3 | -17 |
| NaOH 2M | H ₂ O/Si = 3 | -10 |
| HCOOH 85% | HCOOH/Si = 3 | -14.5 |
| HCOOH 85% | HCOOH/Si = 6 | -14.5 |

antisymmetric stretches, while the band at 695 cm^{-1} is assigned to the Si—O—Si symmetric stretch. The broad band with a maximum at $\approx 3500 \text{ cm}^{-1}$ is ascribed to stretching of the OH of the Si—OH groups that are hydrogen-bonded, plausibly, to O=C groups. No band near 3690 cm^{-1} is observed for free OH of the Si—OH groups. A small band at 904 cm^{-1} , derived from the Si—OH stretch, was present in the products obtained after the 48 h at 40°C but could not be detected in the final material, meaning that a high degree of condensation was achieved with the selected catalysts and thermal cycle. However, the glass transition temperature of the reaction products was close to the value of the starting oligomer (Table I).

To obtain SiOH-functionalized oligomers, it was necessary to select mild conditions for the hydrolytic condensation. The process was carried out in two steps: The first one was performed in THF (1.5 g/mL), using HCOOH 0.1N as a catalyst with a ratio H₂O/Si = 3, for 24 h at 50°C (after

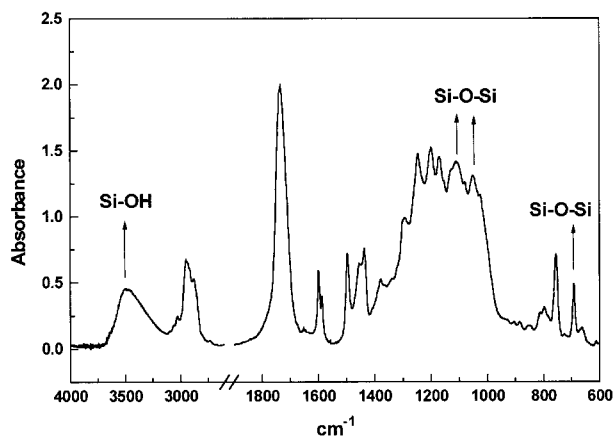


Figure 8 FTIR spectrum of the product resulting from the hydrolytic condensation process carried out at increasing temperatures up to 150°C.

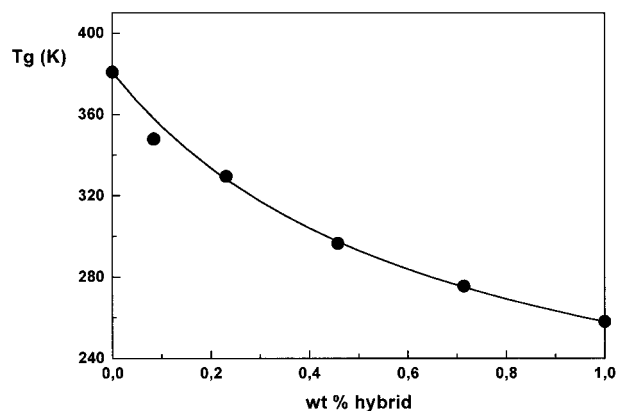


Figure 9 T_g of the modified epoxy network as a function of the mass fraction of the SiOH-functionalized hybrid oligomer. The full line represents the fitting with the Gordon-Taylor equation with $k = 2.5$.

this time, the hydrolysis of the SiOCH₃ groups was carried out to completion). Then, in the second step, DGEBA was added as a solvent in an amount that depended on the desired proportion of the SiOH-functionalized oligomer in the epoxy network. The condensation was advanced during a 24-h period, at 70°C, during which the remaining amount of THF was eliminated. SEC chromatograms showed that only oligomers were obtained after this step.

Epoxy/Anhydride Networks Modified by SiOH-functionalized Oligomers

A stoichiometric amount of MTHPA together with the initiator (BDMA) were added to the DGEBA solution containing the SiOH-functionalized oligomer. The polymerization was carried out at 70°C (24 h), followed by a postcure step where the temperature was increased in steps up to 140°C and kept at this value for 6 h. Transparent glassy materials were obtained with no evidence of phase separation.

The polymerization was also followed by DSC. The reaction heat was between 50 and 55 kJ/eq, in the same range of values reported in the literature.^{8,9} This means that epoxy groups of DGEBA remained unaltered during the hydrolysis and partial condensation of the oligomer.

Epoxy/anhydride networks containing different mass fractions of the SiOH-functionalized oligomer ($f_{\text{GPMS}} = 0.5$) were obtained. Figure 9 shows the T_g of the plasticized epoxy networks as a function of the mass fraction of the SiOH-functionalized hybrid oligomer.

Table II Properties of the Epoxy Modified with 23 wt % SiOH-functionalized Oligomer and of the Neat Matrix

| Property | Modified Epoxy | Neat Matrix |
|---------------------|----------------|-------------|
| T_g (K) | 330 | 381 |
| E (GPa) | 1.3 | 3.4 |
| σ_{yc} (MPa) | 50 | 135 |
| Microhardness (GPa) | 4.5 | 5.5 |
| Abrasion Resistance | 1.44 | 1 |

The Gordon–Taylor copolymer equation¹⁰ was used to fit the experimental curve:

$$(T_{gE} - T_g) = kw_H(T_{gE} - T_{gH})/[1 + w_H(k - 1)] \quad (5)$$

where $T_{gE} = 381$ K is the glass transition temperature of the neat epoxy matrix, $T_{gH} = 258$ K and w_H are, respectively, the glass transition temperature and the mass fraction of the SiOH-functionalized oligomer, and k is a constant defined as

$$k = (\beta_R - \beta_G)_H / ((\beta_R - \beta_G)_E) \quad (6)$$

where β is the first derivative of the specific volume with respect to temperature and R and G refer to the rubbery and glassy states, respectively. When $k = T_{gE}/T_{gH} = 1.47$, the Gordon–Taylor equation becomes equivalent to the Fox equation¹¹:

$$1/T_g = w_E/T_{gE} + w_H/T_{gH} \quad (7)$$

A reasonable good fitting was obtained using the Gordon–Taylor equation with $k = 2.5$ (Fig. 9). For an epoxy resin plasticized by an internally epoxidized polybutadiene rubber, a value of $k = 2.0$ was reported.^{12,13} An increase in the k value corresponds to an increase in $T_{gE} - T_g$ (higher plasticization effect).

Let us assume that a T_g of 330 K is acceptable for a particular application of the plasticized epoxy, for example, for a coating, adhesive, or sealant. This T_g is obtained by introducing 23 wt % of the SiOH-functionalized oligomer in the initial mixture (Fig. 9). Different properties of this particular formulation were measured and compared with those of the neat epoxy matrix. Table II shows the results.

Both the elastic modulus and the yield stress in compression decrease significantly in the plasti-

cized material. A small decrease is also observed in the microhardness, but, as a counterpart, the abrasion resistance increases significantly. This seems to be one of the better characteristics of the modified material. Besides, the presence of free SiOH groups may be used to provide good adhesion with glass surfaces.

CONCLUSIONS

SiOH-functionalized oligomers were synthesized by the hydrolysis and partial condensation of epoxy/anhydride oligomers containing trialkoxysilane groups. Solutions of these oligomers in a liquid epoxy were cured with a stoichiometric amount of an anhydride using a tertiary amine as an initiator. The resulting materials showed no evidence of phase separation, a better abrasion resistance than that of the neat matrix, and a potentially good adhesion with glass surfaces due to the presence of free SiOH groups.

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REFERENCES

- Matejka, L.; Lövy, J.; Pokorny, S.; Bouchal, K.; Dusek, K. *J Polym Sci Polym Chem Ed* 1983, 21, 2873.
- Dusek, K. *Adv Polym Sci* 1986, 78, 1.
- Mauri, A. N.; Galego, N.; Riccardi, C. C.; Williams, R. J. *J. Macromolecules* 1997, 30, 1616.
- Graf, R. T.; Koenig, J. L.; Ishida, H. *Anal Chem* 1984, 56, 773.
- Ishida, H.; Koenig, J. L. *Appl Spectrosc* 1978, 32, 462.
- Miller, J. D.; Ishida, H. *J Chem Phys* 1987, 86, 1593.
- Antonucci, J. M.; Fowler, B. O.; Stansbury, J. W. *Polym Prepr Am Chem Soc* 1997, 38, 118.
- Bouillon, N.; Pascault, J. P.; Tighzert, L. *J Appl Polym Sci* 1989, 38, 2103.
- Corcuera, M. A.; Mondragon, I.; Riccardi, C. C.; Williams, R. J. *J Appl Polym Sci* 1997, 64, 157.
- Gordon, M.; Taylor, J. S. *J Appl Chem* 1952, 2, 493.
- Fox, T. G. *Bull Am Phys Soc* 1956, 1, 123.
- Bussi, P.; Ishida, H. *Polymer* 1994, 35, 956.
- Bussi, P.; Ishida, H. *J Polym Sci B Polym Phys* 1994, 32, 647.