# Self-Curable Polyester by a Reaction of Glycidol with Maleic Anhydride

### NIYAZI BICAK, BUNYAMIN KARAGOZ, UMIT TUNCA

Department of Chemistry, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

Received 8 May 2003; accepted 2 June 2003

ABSTRACT: The controlled reaction of equimolar quantities of maleic anhydride and glycidol in dimethoxyethane gives soluble polyesters with one hydroxyl group in each repeating unit. The reaction proceeds with stepwise ring opening of the components and gives highly viscous clear solutions in relatively short periods. In the first step, monomaleate ester formation takes place around 80 °C. The ring opening of the oxirane group is the second step, and it occurs at 120 °C. The overall reaction is the formation of soluble polyesters with moderate molecular weights (6000–18,000), without the elimination of water. The soluble polyesters can be crosslinked tightly by direct heating at 190 °C without additional vinyl monomer. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 2549–2555, 2003

Keywords: 1-hydroxy-2,3-epoxy propane; maleic anhydride; unsaturated polyesters

## INTRODUCTION

Maleic anhydride (MA) is one of the most important compounds for the preparation of unsaturated polyesters. The presence of maleic ester segments in copolyesters provides dye reception and postcrosslinking abilities. The high electron deficiency of MA makes it capable of charge-transfer interactions. Although MA itself is a nonhomopolymerizable monomer, it forms alternating copolymers with other vinyl monomers, such as styrene<sup>1</sup> and vinvl acetate.<sup>2</sup> because of its chargetransfer-forming ability. Similarly, maleate ester segments in unsaturated polyesters can be copolymerized with styrene monomer to give crosslinked polymers. This reaction has a widespread application for the hardening of polyesters.<sup>3,4</sup> Polyesters obtained from MA or maleic acid contain both maleate and fumarate double bonds because of the isomerization of maleic acid semiesters during polycondensation at elevated

temperatures.<sup>5</sup> Because the fumarate double bond has a much greater reactivity in copolymerization with vinyl monomers, unsaturated polyesters with high fumarate contents undergo rapid crosslinking with styrene.<sup>6</sup>

The double bond of maleate ester, however, has a remarkable reactivity toward the nucleophilic addition of —NH, —SH, or —OH groups. The acid-catalyzed addition of hydroxyl groups to the double bonds causes the formation of branching points with ether linkages<sup>7</sup> under polyesterification conditions.

The reaction of bisepoxy compounds with dicarboxylic acids to give linear polyesters has been described in the literature.<sup>8</sup> This reaction has been employed for the preparation of polyesters with hydroxyl groups. This approach has also been applied to the crosslinking of hyperbranched polyacids.<sup>9</sup> An interesting method related to polyester formation is the reaction of epoxy groups with cyclic anhydrides.<sup>10,11</sup> The reaction proceeds without water elimination and takes place under mild conditions in the presence of tertiary amine catalysts.

Correspondence to: N. Bicak (E-mail: bicak@itu.edu.tr) Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 41, 2549–2555 (2003) © 2003 Wiley Periodicals, Inc.

This study is aimed at the preparation of linear polyesters by a reaction of MA with glycidol (GL). The anhydride component is expected to react first, whereas the epoxy group of GL must react at higher temperatures. If the reaction proceeds step by step, linear polyesters with hydroxyl pendant groups can be prepared. The resulting hydroxyl group would be beneficial for imparting some hydrophilicity to the polyesters.

Because an additional hydroxyl group forms by the ring opening of the epoxy function, GL can be considered a potential 3-hydroxyl compound. Therefore, a reaction of GL with MA is reminiscent of the polycondensation of a trihydric alcohol with a dicarboxylic acid yielding network polyesters. The possibility of linear polyester formation in such a cause depends not only on the temperature profile and stoichiometry but also on the reactivity differences between epoxy and hydroxyl groups in ester formation.

In this work, we have targeted the preparation of soluble polyesters from MA and GL. The resulting polyesters have been characterized with <sup>1</sup>H NMR and gel permeation chromatography (GPC). Moreover, the crosslinking ability of the soluble polyesters by thermal curing and crosslinking copolymerization with styrene has been studied.

### **EXPERIMENTAL**

### Materials

Dimethoxyethane (Fluka) was distilled before use. Styrene (Merck) was made inhibitor-free by being shaken with a 5% aqueous NaOH solution and dried with anhydrous  $Na_2SO_4$ . All other chemicals were analytical-grade commercial products [MA from Merck and GL (1-hydroxy-2,3epoxy propane) from Acros Chemicals] and were used as obtained.

#### Measurements

<sup>1</sup>H NMR spectra were recorded on a Bruker 250-MHz spectrometer with acetone- $d_6$  as a solvent and tetramethylsilane (TMS) as an internal standard. GPC measurements were taken with an Agilent 1100 with a refractive-index detector equipped with Waters Styragel columns (HR 5E, HR 4E, HR 3, and HR 2). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.3 mL/min at 30 °C. The molecular weight of the polymers was calculated with the aid of polystyrene standards. Differential scanning calorimetry (DSC) thermograms were taken with a PerkinElmer DSC 6 instrument (at a heating rate of 5 °C/min under nitrogen)

### Synthesis of Monoglycidyl Maleate

The first-step product of the MA–GL reaction was obtained as a waxy product as follows: 3.7 g ( $5 \times 10^{-2}$  mol) of GL (2,3-epoxy-1-propanol), 4.9 g ( $5 \times 10^{-2}$  mol) of MA, and 4 mL of dimethoxyethane (ethylene glycol dimethyl ether) were placed in a 50-mL flask. The flask was mounted in a thermostated oil bath at 70 ± 3 °C. The mixture was stirred for 45 min. After cooling, the contents of the reaction were poured into *n*-heptane or diethyl ether (30 mL). The white precipitate was separated by decantation. The residue was dissolved in 4 mL of dimethoxyethane and reprecipitated in diethyl ether. The resulting product was dried at 40 °C *in vacuo* for 24 h. The yield of the waxy product was 7.3 g (84.9%).

### **Determination of the Carboxyl Content**

The carboxyl content of the product was determined by conductometric titration with a 0.1 M NaOH solution. The product (0.67 g) was dissolved in water and diluted to 100 mL in a volumetric flask, and 50 mL of this solution was titrated with a 0.1 M NaOH solution. The titrant (19.1 mL) consumed corresponded to 5.7 mmol of carboxylic groups per gram of the product. The theoretical value expected for the monoglycidyl maleate (molecular weight = 172) was about 5.813 mmol g<sup>-1</sup>. The ratio of the two [(5.7/5.813) = 0.98] was very close to unity. The <sup>1</sup>H NMR spectrum of the product is given later in Figure 2(a).

# Preparation of the Soluble Polyester from MA and GL

The polyesterification of MA with GL was carried out either by stepwise heating at 70 and 120  $^{\circ}$ C (method A) or by direct heating at 120  $^{\circ}$ C (method B).

### Method A

MA (24.5 g, 0.25 mol) was dissolved in a mixture of GL (18.5 g, 0.25 mol) and dimethoxyethane (15 mL) in a reaction flask equipped with a reflux condenser and  $CaCl_2$  guard tube. The flask was



Scheme 1. Synthesis of the self-curable polyester.

placed in a thermostated oil bath preheated at a constant temperature of 70 °C. The mixture was stirred for 45 min. The temperature of the oil bath was adjusted to 120 °C, and stirring was continued for another 45 min. The viscosity of the mixture gradually increased. The flask was then removed from the oil bath and cooled to room temperature. The resulting viscous solution was optically clear, and no significant viscosity change was observed after it was left in a closed bottle for a week at room temperature. The <sup>1</sup>H NMR spectrum of the polymer is given later in Figure 2. The intrinsic viscosity of the polyester in dimethoxyethane was  $0.034 \text{ dL g}^{-1}$ . GPC indicated a number-average molecular weight  $(M_n)$  of 16,400 and a weight-average molecular weight  $(M_w)$  of 17,200 (shown later in Fig. 3). The product was soluble in water, ethanol, acetone, dimethylformamide (DMF), and THF and insoluble in benzene, toluene, ether, and *n*-heptane.

### Method B

The same procedure was followed, except that the mixture was heated at 120 °C for 45 min. The polymers obtained by heating for prolonged times were partly soluble in water.

# **RESULTS AND DISCUSSION**

The controlled reaction of MA with GL in dimethoxyethane gives soluble polyesters (Scheme 1). Because polyester formation in this reaction proceeds without water elimination, highly viscous and clear solutions can be obtained within reasonably short periods, that is, 2–3 h. The reaction without a solvent, however, always results in crosslinked insoluble products. Many attempts at preparing soluble polyesters without a solvent failed. This must be due to the exothermic nature of the reaction. In this case, heat dissipation by stirring becomes almost impossible because of the increasing viscosity of the mixture, and a sudden rise in the temperature leads to further reactions yielding crosslinked structures. Therefore, the use of a solvent is essential for preparing soluble polyesters.

The polyester formation proceeds in two steps: (1) the reaction of MA with the hydroxyl group of GL and (2) the ring opening of the epoxy group to react with the free carboxyl group. The two-step mechanism is supported by DSC. DSC traces of an MA–GL mixture (Fig. 1) show two exothermic peaks below 150 °C. The peaks observed at 80 and



Figure 1. DSC traces of an MA–GL mixture (heating rate = 10 °C/min; N<sub>2</sub> atmosphere).

120 °C must be associated with the first and second steps, respectively. To prove this assumption, we have compared DSC thermograms of MA/*n*butanol and GL/phthalic acid mixtures with those of the MA–GL mixture. However, the MA/*n*-butanol and GL/phthalic acid mixtures gave exothermic peaks at 100 and 110 °C. Although the monoesterification temperature of MA is somewhat lower than that of the ring opening of the epoxy group, this result is not satisfactory for making such an assignment.

Nevertheless, the stepwise reaction scheme is verified by the isolation of the first-step product formed at 80 °C. The isolation of this reaction intermediate is very difficult because of a sudden rise in the reaction temperature. This is achieved by the adjustment of the bath temperature at 70 °C. The inner temperature of the equimolar MA-GL mixture in dimethoxyethane, under these conditions, reaches around 80 °C because of the contribution of the heat evolving from the exothermic reaction. Vigorous stirring for 45 min and subsequent precipitation in ether give a white, waxy product. Attempts at the crystallization of this product failed. However, conductometric titration of the product (with 0.1 M NaOH) indicates a 98% pure monocarboxyl compound. Also, the <sup>1</sup>H NMR spectrum of this intermediate [Fig. 2(a)] reveals the monoglycidol maleate structure.

These results reveal that the polymerization proceeds by a two-step reaction scheme and that the first step occurs at 80 °C and gives monoglycidol maleate. As a result, a linear polyester can be prepared either by heating in two steps at 70 and 120 °C or by direct heating at 120 °C. Indeed, both procedures give soluble polyesters when equimolar mixtures of MA and GL are reacted in aprotic solvents such as dimethoxyethane, DMF, and *N*-methylpyrrolidone. Having a low boiling temperature, dimethoxyethane is a better solvent.

The formation of the monoglycidyl maleate intermediate and subsequent polyesterification can be followed by NMR spectra of the corresponding products. Therefore, the <sup>1</sup>H NMR spectrum of the intermediate [Fig. 2(a)] establishes the monoglycidyl maleate structure. Nonequivalent protons of the maleate groups can be observed at 6.4 and 7.4 ppm. Other aliphatic proton signals are located in the 3.3–4.3 ppm range. The integral ratio of these group signals is 1/3, as expected, whereas carboxyl protons do not give a visible peak or band as usual. The <sup>1</sup>H NMR spectrum of the soluble polyester prepared in dimethoxyethane [Fig. 2(b)] shows a single peak for equivalent protons of maleic double bonds at 7.1 ppm. This is clear-cut evidence for the polymerization of monoglycidyl maleate. A new signal emerging at 2.7 ppm in Figure 2(b) is due to the methine protons of the carbinol group resulting from ring opening of the oxirane function.

The integral ratios of those peaks are also consistent with the structure of the polyester proposed. However, it is difficult to make an assignment for the maleate-fumarate isomer ratio on the basis of the location of the proton signal of the double bond because the proton signal of the fumarate isomer does not appear around 6.8 ppm. With respect to the lower field shift of the double-bond protons, one can assume that the signal at 7.1 ppm originates mostly from the maleate structure. Such an isomerization is most likely being prevented by the controlled process. These results clearly indicate that soluble polyesters can be prepared by controlled reactions in dimethoxyethane.

A GPC trace of the polyester (Fig. 3) obtained by heating at 120 °C in dimethoxyethane for 1 h indicates an  $M_n$  value of 6200 with a polydispersity index of 1.01. The intrinsic viscosity of this product was 0.12 dL g<sup>-1</sup>.

For the correlation of the intrinsic viscosities with the molecular weight data (from GPC), the Mark–Houwink parameters of the polyester were estimated as follows:

$$K = 7.4 \pm 0.1 imes 10^{-4}$$

 $a = 0.42 \pm 0.02$  (in dimetoxyethane at 30 °C)

Many polymers with different viscosities can be prepared, depending on the reaction periods. However, 2 h is enough to obtain polyesters with appreciable viscosities. Of course, one can obtain polyesters of different molecular weights with various solvent ratios in different reaction times (Table 1). The molecular weights attained are proportional to the reaction times.

In this work, we have not attempted to make an optimization for preparing polyesters with predetermined molecular weights.

Because esterification of the free hydroxy group with the carboxyl group is less favorable at 120 °C, the polymerization must take place via ring opening of the oxirane function at this temperature. As a result, the formation of linear poly-





**Figure 2.** <sup>1</sup>H NMR spectra of (a) monoglycidyl maleate and (b) the polyester obtained by the heating of the MA–GL mixture at 115 °C for 45 min in acetone- $d_6$  with TMS as an internal standard.

ester becomes predominant. Although it is difficult to assign a linear structure based on the NMR spectra, linearity seems to be more likely. In such a case, epoxy and carboxyl groups must be retained at the chain ends after the reaction. Indeed, the prolonged heating of the viscous polymer solutions causes a rise in the viscosities, which indicates the presence of the reactive groups at the chain ends. For instance, the heating of a sample polyester solution for 1 h more at 120 °C results in increases in  $M_n$  from 6200 to 13,200. This can be ascribed to chain extension of the polyester by the continued reaction of the



Figure 3. GPC trace of the polyester (sample 1) in THF as a solvent (flow rate = 0.3 mL/min).

		Reaction Time				
Sample	Monomer Ratio (w/w) <sup>a</sup>	At 70 °C <sup>b</sup>	At 120 °C <sup>b</sup>	Limit Viscosity <sup>c</sup>	${M_{ m n}}^{ m d}$	$M_{ m w}/M_{ m n}$
1	86	_	120	0.037	11,700	1.06
2	90	_	60	0.049	22,700	1.04
3	90	90	30	0.034	16,400	1.05
4	90	90	60	0.045	17,500	1.01

**Table 1.** Characteristics of Soluble Polyester Formation

<sup>a</sup> Percentage of the total mass of the monomers.

<sup>b</sup> Bath temperature.

<sup>c</sup> Intrinsic viscosity in dimethoxy ethane at 30  $\pm$  1 °C.

<sup>d</sup> GPC with THF as an eluent calibrated with polystyrene standards.

epoxy groups at the chain ends. Unfortunately, we were not able to make a quantitative determination of the terminal oxirane groups by the pyridinium chloride method. However, this observation supports the structure of the polyester depicted in Scheme 1.

Because the reaction is fast enough in this study, we have not dealt with the kinetics of polyesterification. The overall results reveal that soluble polyesters can be prepared by a controlled reaction in dimethoxyethane. The resulting polyester with one hydroxyl group in each repeating unit is highly adhesive for various substrates, such as metals and wooden goods, and is useful for postcuring. Apparently, the OH groups involved provide adhesiveness to the product.

## Crosslinking

The crosslinking of the polyester can be achieved by either thermal curing or crosslinking copolymerization with styrene monomer (Scheme 2). A hard and insoluble material is obtained in each case. The optimum cure temperature for the crosslinking of the polyester can be predicted from the DSC curve. The first two-step sharp exotherms of the MA–GL mixture are absent in the DSC trace of the soluble polyester [solvent-



**Scheme 2.** Crosslinking of the polyester by thermal curing and crosslinking copolymerization with styrene.



**Figure 4.** Soluble fractions of the polyesters cured at 190 °C.

free; Fig. 1(b)]. This fact is more evidence for the two-step mechanism. In the DSC graph of the polyester, a broad endotherm at 180–220 °C and an intense exothermic band centered at 350 °C can be ascribed to self-crosslinking and decomposition, respectively. For the MA–GL mixture, the endothermic peak is not clear, and a slight depletion in this range cannot be ascribed to an endothermic peak, most likely because of a fast scan rate (10 °C/min) of the temperature in comparison with the reaction rate at the second step.

On the basis of these considerations, we tested the self-curing ability of the polyester by thermal curing at 190 °C for different time intervals. The efficiency of the curing was followed by an inspection of the soluble portions of the cured samples in acetone. There was no mass change of the samples cured for over 3 h, as represented in Figure 4. Here, thermal crosslinking must be due to the addition of hydroxy groups to the maleic double bonds to form ether linkages. This result agrees with reports in the literature.<sup>7</sup> A C—O stretching vibration associated with the ether linkage can clearly be observed at 1080 cm<sup>-1</sup> in the IR spectra of the cured samples. Therefore, this polymer is a self-crosslinkable material that would be beneficial for various applications.

Moreover, copolymerization with styrene is also an efficient method of crosslinking. However, pure polyester is not miscible with styrene. The addition of a small amount of THF gives a homogeneous mixtures. A mixture with 2 equiv of styrene undergoes crosslinking in about 35 min when heated with benzoyl peroxide at 85 °C. In this work, we have not studied the details of curing with styrene. Obviously, styrene-based curing procedures are also applicable for this polyester.

### CONCLUSIONS

A soluble polyester with pendant hydroxyl groups can be prepared by the controlled heating of an MA–GL mixture in dimethoxyethane as a solvent. Without a solvent, the reaction yields crosslinked products. The hardening of the soluble polyester can be achieved by crosslinking copolymerization with styrene. The soluble polyester is an adhesive for metals and cellulose-based materials because of the hydroxyl functions involved. Having such peculiarities, the presented soluble polyester seems to be especially suitable for spray-coating applications. Further studies devoted to coatings are under consideration.

### **REFERENCES AND NOTES**

- 1. Mathew, A.; Deb, P. C. J Polym Sci Part A: Polym Chem 1996, 34, 1605.
- Spridon, D.; Panaitescu, L.; Ursu, D.; Uglea, C. V.; Popa, I.; Ottenbrite; R. M. Polym Int 1997, 43, 175.
- Sanchez, E. M. S. A.; Zavaglia, C. A. C.; Felisberti, M. I. Polymer 2000, 41, 765.
- Mayo, F. R.; Lewis, F. M.; Walling, C. J Am Chem Soc 1948, 70, 1529.
- 5. Hsu, C. P. A.; Lee, L. J. Polymer 1991, 32, 2263.
- 6. Grobelny, J. Polymer 1995, 36, 4215.
- 7. Ordelt, Z. Macromol Chem 1963, 63, 153.
- 8. Tanaka, Y.; Kakiuchi, H. J Polym Sci Part A: Gen Pap 1964, 2, 3405.
- 9. Liu, H.; Wilen, C. E.; Skrifvars, M. J Polym Sci Part A: Polym Chem 2000, 38, 4457.
- Trappe, V.; Burchard, W.; Steinmann, B. Macromolecules 1991, 24, 4838.
- 11. Steinmann, B. J Appl Polym Sci 1990, 39, 2005.