

Copolymerization of Trioxane with the Diglycidylether of 1,4-Dihydroxy-Diphenyl-Dimethyl-Methane

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SYNOPSIS

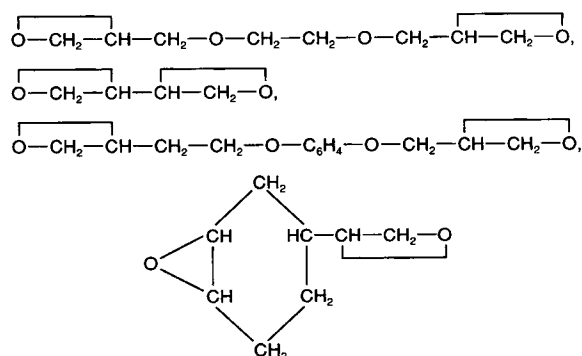
The copolymerization of trioxane (TO) (100 mol %) with the diglycidyl ether of 1,4-dihydroxy-diphenyl-dimethyl-methane (DE-Ph) (5–25 mol %) catalysed by BF_3OEt_2 in nitrobenzene was studied. The kinetics of the polymerization process was followed gravimetrically and dilatometrically in the temperature range of 30–60°C. It was established that no homopolymers were formed. The copolymers obtained show high alkaline and thermal stability. The copolymerisation is inhibited at increased DE-Ph levels. The copolymers were characterised also by their infrared (IR) spectra and differential scanning calorimetry (DSC).

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INTRODUCTION

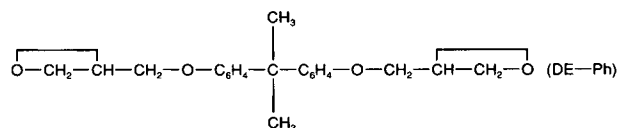
A great number of trioxane (TO) copolymers with epoxy compounds (i.e., ethylene oxide, propylene oxide, epichlorohydrin, glycidylether, phenylglycidylether) have been studied and reported in the literature.^{1–3}

The number of TO copolymers with diepoxy derivatives is relatively limited. There is evidence concerning copolymerization of TO with the following scheme³:



These compounds are usually used in quantities of 0.5–1% so that branching and cross-linking are avoided. Emphasis was given to the study of melt

index, thermal stability, yield, and molecular weight of the copolymer. No reports have been found in the literature on the copolymerization of TO with the diglycidylether of 4,4 dihydroxydiphenyl-dimethyl-methane (DE-Ph).



The present work aims to clarify the questions concerning the copolymerization of TO and DE-Ph. The effect of the incorporated DE-Ph units on the super molecular structure and on the thermal stability of the obtained copolymer of TO and DE-Ph was of interest.

Investigations of DE-Ph copolymers were carried out with the aim of finding out the peculiarities and regularities of the copolymerization process. Kinetic studies have also been made.

EXPERIMENTAL

The copolymerization of TO with DE-Ph was carried out in nitrobenzene solution in the presence of the initiator $\text{BF}_3\text{Et}_2\text{O}$ in argon atmosphere at temperatures of 30–60°C. The TO used was a Fluka product. The isolation and purification of the co-

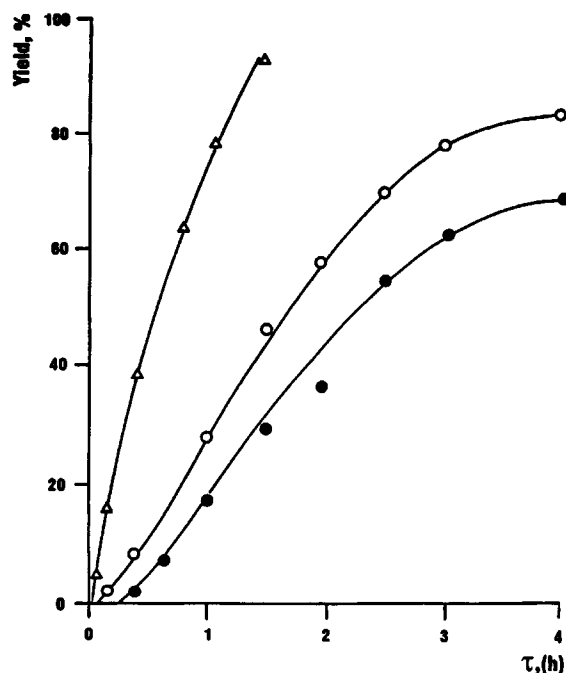


Figure 1 Conversion of TO to POM ($-\Delta-$) and of TO and 5 mol % ($-\circ-$) or 10 mol % ($-\bullet-$) DE-Ph. Polymerization is carried out at 60°C with an initiator $\text{BF}_3\text{Et}_2\text{O}$ in amount of $4 \cdot 10^{-3}$ g/mol per g/mol monomers.

polymers were realized according to well known methods.⁴ DE-Ph was synthesized according to French Patent 7638120.⁵

The thermal stability was determined by thermogravimetric analysis with a Perkin Elmer-2 apparatus, at a heating rate 20°C/min. The thermal behaviour of the copolymers was determined by differential scanning calorimetry (DSC) with a Perkin Elmer apparatus at a heating rate of 20°C/min. The isolated and purified copolymers were studied and examined for alkaline resistance by a method described in the literature.⁶ The copolymers were characterized by IR-spectra recorded with a Perkin Elmer 180 spectrometer in KBr pellets. The molecular weights were determined by the viscosimetric method in a solution of phenol-tetrachloroethane at 90°C using a 0.6 mm capillary according to eq. 1.⁷

$$\eta = 5.2 \times 10^{-1} \bar{M}_v^{0.93} \quad (1)$$

The molecular weights were determined immediately after the preparation of the solutions. The determination of the molecular weights of copolymers containing above 15% of DE-Ph according to eq. (1) is not very accurate because of the high content of DE-Ph. The formula used is valid for the determination of molecular weights of TO homo-

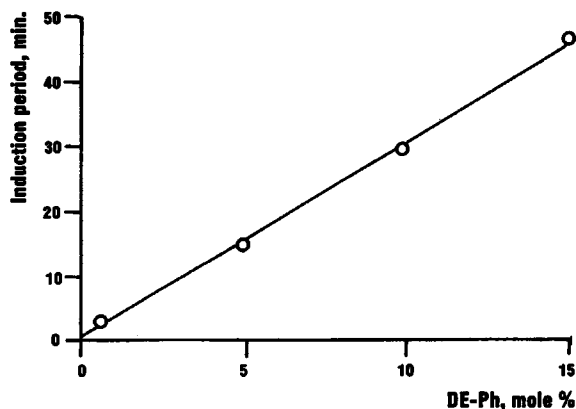


Figure 2 Dependence of the induction period of copolymerization of TO/DE-Ph mixtures on the DE-Ph content. Reaction conditions are the same as in Figure 1.

polymers and for copolymers containing approximately up to 10 mol % comonomer.

The chain transfer constants were determined according to the following equation.⁸

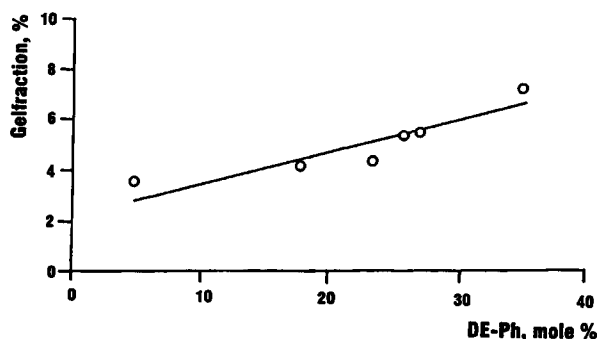
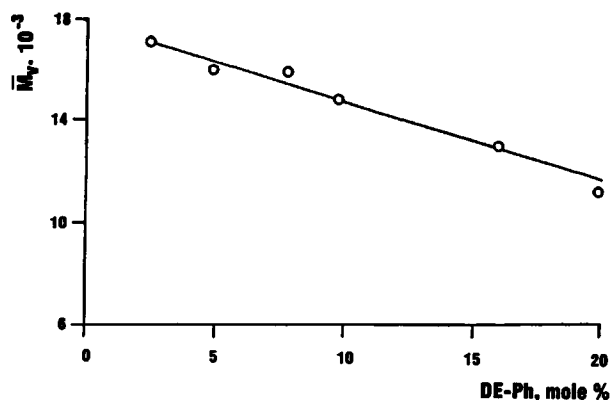


Figure 3 (a) Influence of the DE-Ph amount (mol %) included in the copolymer on the average molecular weight \bar{M}_v . (b) Dependence of the amount of the gel fraction (%) of TO/DE-Ph copolymers on their DE-Ph content (mol %). Copolymerization conditions are the same as in Figure 1. Reaction time is 4 h.

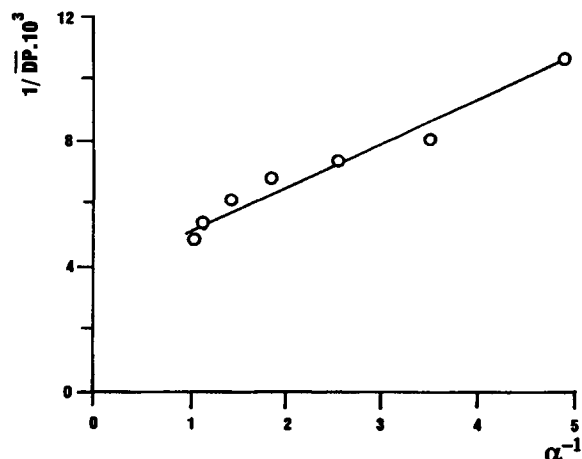


Figure 4 Dependence of the reciprocal value of the degree of conversion (α) on the reciprocal value of the degree of copolymerization (DP) of TO and DE-Ph. Reaction conditions are the same as in Figure 1. Reaction time is 4 h.

$$DP^{-1} = \frac{[C] \text{ "live" }}{2 \times \alpha \times [M]} + \frac{K_{tr}}{K_p + K_{tr}} \quad (2)$$

where $[C]$ "live" is the concentration of the "live" ends;

$$\frac{K_{tr}}{K_p + K_{tr}} = K'_{tr} \text{ is the transfer constant;}$$

$\alpha = \text{yield \%} / 100$ is the degree of conversion

RESULTS AND DISCUSSION

The copolymerization of TO with DE-Ph in a molar ratio of 5 : 25 was a heterogeneous process since the copolymer obtained separated in the form of a white insoluble precipitate. The conversion curves have an exponential character (Fig. 1). It was established that the polymerization rate decreases while the induction period increases with the rise of the DE-Ph content in the monomeric starting reaction mixture (Fig. 2).

With the increase of DE-Ph concentration in the initial monomeric mixture, not only was a decrease of the extent of conversion observed, but also a decrease of the molecular weight [Fig. 3(a)] with a simultaneous increase of gel fraction percentage [Fig. 3(b)].

The increase of the gel fraction with the increase of DE-Ph [Fig. 3(b)] could be easily explained with the possibility of a bicerated growth mechanism because of the bifunctionality of DE-Ph. It can be

expected that the two epoxide rings of DE-Ph react via the tertiary oxonium ion.⁹

The kinetic investigations were carried out by both methods, dilatometrically as well as gravimetrically.

The decrease of the average molecular weight (\bar{M}_v) [Fig. 3(a)], as well as the results shown in Figure 4 of the relationship DP^{-1}/α^{-1} according to the Pepper equation⁸ [see Eq. (2)], definitely indicate that DE-Ph participates in reactions of transfer and breaking of the chain. The section of the ordinate determines the transfer constant $K_{tr} = 0.38 \cdot 10^{-4}$ mol/l/s.

Figures 5 and 6 show that the alkaline and thermal stabilities of the copolymers increase with increasing DE-Ph amount included in the polyoxymethylene (POM) chains. These changes were most clearly observed with the copolymers containing 5 mol % of DE-Ph. The introduction of DE-Ph comonomer units in the POM chains results in an abrupt improvement of the thermal and alkaline stability of the copolymers obtained (Figs. 5 and 6).

The bimodality of the thermodegradation curves 2, 3, and 5 is due most likely to different kinds of degradation processes taking place at different temperatures. The range between 50 and 170°C belongs to the first section. The second section is in the range of 170–300°C.

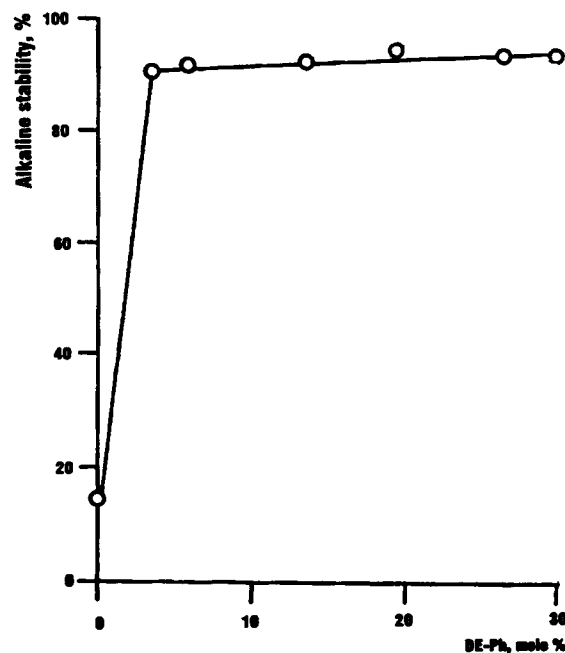


Figure 5 Dependence of the alkaline stability of the TO/DE-Ph copolymer on the amount of DE-Ph inserted (mol %). Reaction conditions are the same as in Figure 1(a). Reaction time is 4 h.

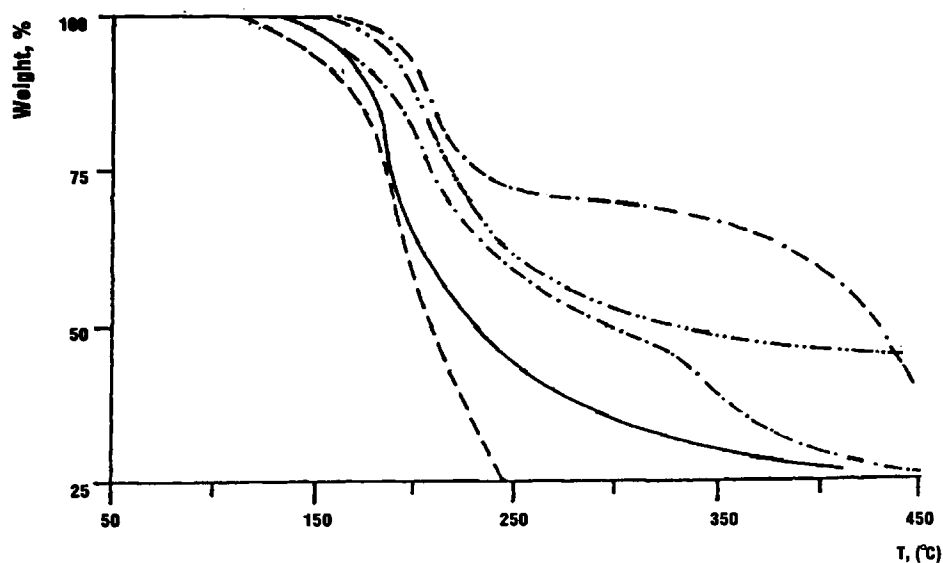


Figure 6 Dependence of the weight losses (%) in TO/DE-Ph copolymers of the heating temperature T ($^{\circ}\text{C}$). POM homopolymer (.....). TO/DE-Ph copolymers with DE-Ph content of 4 mol % (—); 12 mol % (- · -); 25 mol % (- · · -); and 20 mol % (- - -).

In the range of $50\text{--}170^{\circ}\text{C}$, the bond —C—O— is mainly affected. The reaction of destruction is autocatalyzed by the separation of CH_2O ; at higher temperatures ($170\text{--}350^{\circ}\text{C}$), the destruction of —C—C— bonds begins.

The studies concerning the thermal behaviour of the copolymers TO/DE-Ph at melting (Fig. 7),

carried out by DSC, show the existence of two melting points. The first peak lies in the pure polyoxymethylene (POM) region. The second peak lies in the range of $510\text{--}570^{\circ}\text{K}$. The tendency is toward increasing the melting point of the second peak with raising the mol content of DE-Ph. These results could be explained by the assumption of the exis-

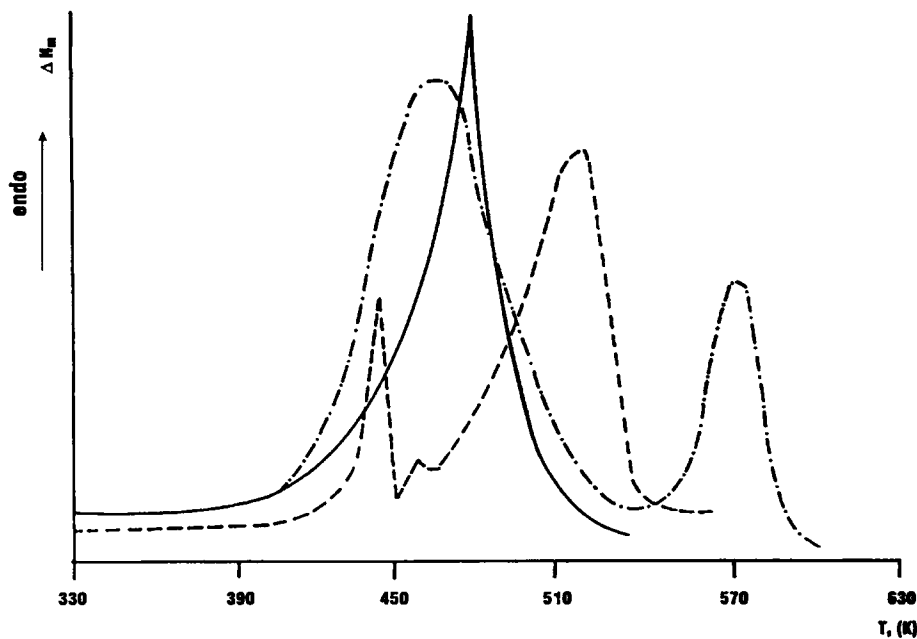


Figure 7 DSC thermograms of POM (—) and TO/DE-Ph copolymers with DE-Ph content of 12 mol % (- - -) and 25 mol % (- · -).

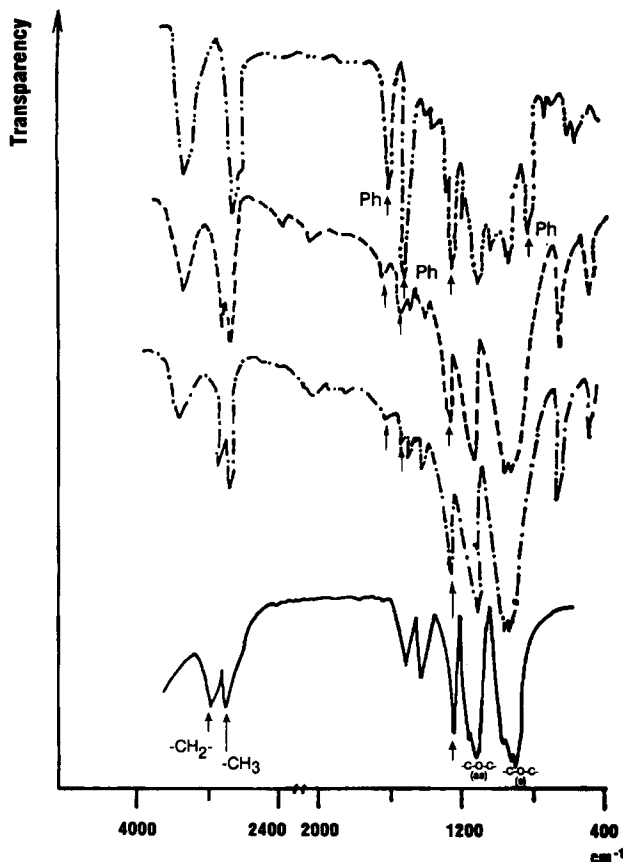


Figure 8 IR spectra of POM (—) and TO/DE-Ph copolymers with DE-Ph content of 12.8 mol % (- · -); 18 mol % (- - -); and 25 mol % (- · · -).

tence of two types of lamellae. The first type lamellae is characterised by a considerable number of DE-Ph units, which are distributed most probably in a block statistical way with a melting peak of 510–570°K. The lamellae of the second type contain fewer units of DE-Ph, incorporated in the stretched part of the chain, with a melting peak of 420–460°K.

The enthalpy of melting should diminish abruptly with the increase of DE-Ph content in the copolymer. In reality, this was not observed with the diagrams of the DSC calorimeter because of a curing process taking place parallel to the melting of crystal sections (Fig. 7).

The recorded IR spectra (Fig. 8) prove that a copolymer of TO and DE-Ph is really present, which is also confirmed indirectly by the alkaline and thermal stabilities (Figs. 5, 6). The absorption bands are clearly outlined in the spectrum at 1590 and 1620 cm^{-1} , corresponding to the oscillations of the aromatic nucleus out-of-plane bending vibrations at 830–840 cm^{-1} , which are characteristic for 1,4 sub-

stitution, and the bands at 1050 and 1150 cm^{-1} , due to the $-\text{C}-\text{O}-\text{C}-$ mode, as well as in the range of 940–960 cm^{-1} . The bands at 3000–3100 cm^{-1} are due to the $\text{C}-\text{H}$ stretching vibrations of the aromatic nuclei but are not treated here because they are observed as a shoulder to the bands due to stretching vibrations of the $-\text{CH}_2-$ groups. The peak at 1235 cm^{-1} illustrates the degree of crystallinity of POM. With incorporation of comonomer units of DE-Ph in the POM chain, the degree of crystallinity should decrease and the peak intensity at 1235–1240 cm^{-1} will also diminish. In our case, the stretching vibration of the group $-\text{C}-\text{O}-\text{C}=\text{C}$ (DE-Ph) appears at 1250 cm^{-1} , but it overlaps the crystallinity band at 1235 cm^{-1} . For this reason, the peak at 1235–1240 cm^{-1} couldn't be used as a measure of crystallinity degree.

The mole percentages of the incorporated DE-Ph units in a POM chain are calculated on the basis of the elemental analysis.

CONCLUSION

From our investigation, it was established that DE-Ph copolymerized easily with TO by two growth centers via a tertiary oxonium mechanism. In the temperature range of 30–60°C and the quantity of 5–10 mol % of DE-Ph to TO, a linear copolymer of TO/DE-Ph with high alkali and thermal stability could be obtained.

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