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Epoxy-terminated phenolphthalein poly(ether ether ketone) reactive oligomers: cure with 4,4'-diaminodiphenylether

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SUMMARY

Epoxy-terminated phenolphthalein poly(ether ether ketone)s (E-PEKs) of number average molecular weights from 1,200 to 8,400 were cured with 4,4'-diaminodiphenylether (DDE). The cure kinetics was studied by DSC. The values obtained for the activation energy of the cure reaction were comparable to those reported for the curing of epoxy systems. The attained glass transition temperature was dependent on the cure temperature. The properties of both the neat oligomer and the fully crosslinked polymer were a function of the initial molecular weight of the oligomer. For molecular weight ($\bar{M}n$) varying between 1,200-4,500 the glass transition temperature of the fully crosslinked polymer (Tgoo) varies between 206-183 °C as a result of decreasing crosslinked density.

INTRODUCTION

Phenolphthalein poly(ether ether ketone) (PEK-C) was developed by this laboratory, serving as a high performance thermoplastic (1,2). Recently, we synthesized a series of epoxy-terminated phenolphthalein poly(ether ether ketone) (E-PEK) reactive oligomers with different molecular weights (3). The expected advantage of those compounds over the higher molecular weight, linear PEK-C resin lies in their easier processing and improved solvent resistance. In this report, we present some preliminary results of our investigations on the cure of E-PEKs with 4,4'-diaminodiphenylether (DDE) and the properties of the crosslinked polymers.

EXPERIMENTAL

The various epoxy-terminated phenolphthalein poly(ether ether ketone)s with general formula as shown in Fig. 1 prepared from the reaction of hydroxy-terminated phenolphthalein poly(ether ether ketone)s and epichlorohydrin (3) are listed in Table 1. 4,4'-Diaminodiphenylether (DDE) (purity grade: >98%) was used as hardener in stoichiometric ratios epoxide/amine.

E-PEK and DDE were mixed in stoichiometric ratio considering E-PEK as difunctional and DDE as tetrafunctional and dissolved in the

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*To whom correspondence should be addressed smallest possible chloroform. The solvent was removed under vacuum at room temperature.

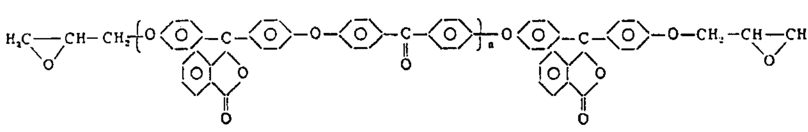

Fig. 1. General formula.

Table 1. Characterization of epoxy-terminated phenolphthalein poly(ether ether ketone)s

Sample	$\bar{M}n$	Tgi (°C)
1	1,200	55
2	1,600	56
3	1,900	80
4	4,400	85
5	4,500	89
6	8,400	214
PEK-C resin	12,000	228*

* from ref. 2.

DSC experiments were run on a Perkin-Elmer DSC-2C differential scanning calorimeter calibrated against indium at a number of heating rates. For each sample the initial glass transition temperature (Tgi) and the glass transition temperature of the partially crosslinked E-PEK/DDE system were measured. To obtain the glass transition temperature of fully cured E-PEK/DDE system (Tg∞), the samples were cured at temperatures above Tg∞ for periods of 8 hours.

RESULTS AND DISCUSSION

All members of the oligomer series are amorphous materials. The initial glass transition temperature (Tgi) is a function of the initial molecular weight ($\bar{M}n$) of the oligomer as illustrated in Table 1. The lower the molecular weight, the lower the initial glass transition temperature. It is noted that the Tgi of sample 6 (214°C) is rather high due to the suitable high molecular weight ($\bar{M}n$=8,400).

Differential scanning calorimetry (DSC) is a valuable technique for determining the curing rate constant and the resulting kinetic parameters (4-6). Fig. 2 shows the dynamic trace for the curing reaction of sample 1 with DDE obtained at 10°C/min. An endothermic peak can be seen at 120°C corresponding to the melting of DDE. Crosslinking occurs before the baseline is recovered; for that reason, the enthalpy values could not be accurately determined and it was not possible to use the isothermal method for cure kinetics study. Nevertheless, the kinetic parameters

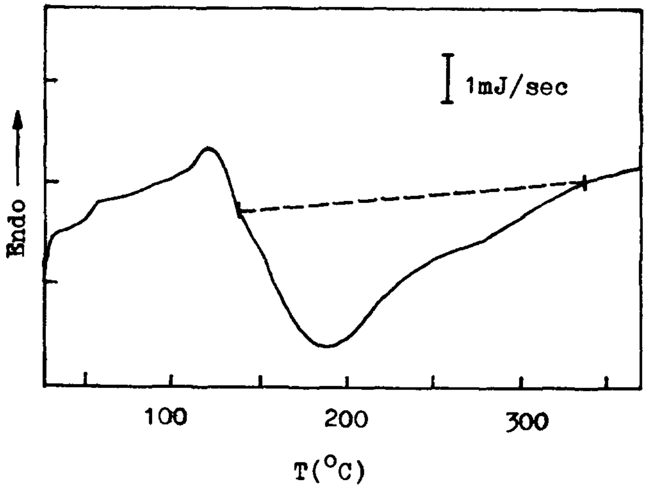

Fig. 2. Dynamic curve at 10°C/min for the curing of sample 1 with DDE.

of cure reaction, such as activation energy, can be determined from a variety of the dynamic DSC traces with different heating rates according to a simple but accurate relationship between activation energy (Ea), heating rate (ϕ) and peak exotherm temperature (Tp) based on work by Ozawa (7,8). By plotting lnϕ vs. 1/Tp at different heating rates (5, 10, 15, 20 and 40°C/min) (Fig. 3) and using the Equation (9,10)

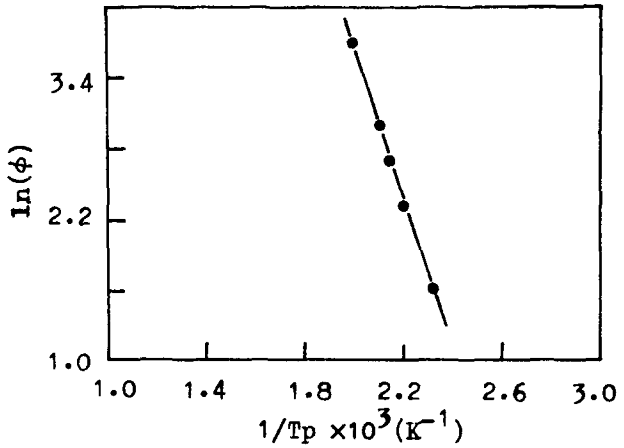

Fig. 3. Determination of the activation energy by dynamic method for the curing of sample 1 with DDE.

$$Ea \simeq -\frac{R}{1.052}\frac{\Delta \ln \phi}{\Delta(1/Tp)}$$

the values of Ea for E-PEKs with DDE were obtained and are listed in Table 2. The data of Ea in Table 2 illustrate a number of noteworthy points: First, the activation energy is independent of the oligomers initial molecular weight; second, it is comparable to the activation energy reported for the curing reaction of common epoxy resins with aromatic diamines (11-14). The E-PEKs with DDE exhibit the same curing behaviour as common epoxy resins with aromatic diamines. Of course, the rates are dependent on the the molecular weight of the oligomer owing to the transport component of the curing reaction.

Table 2. Values of activation energy for the curing reaction of E-PEKs with DDE

Sample	$\overline{Mn}$	Ea (kJ/mol)
1	1,200	66.5
2	1,600	70.4
3	1,900	67.6
4	4,400	68.5
5	4,500	67.0

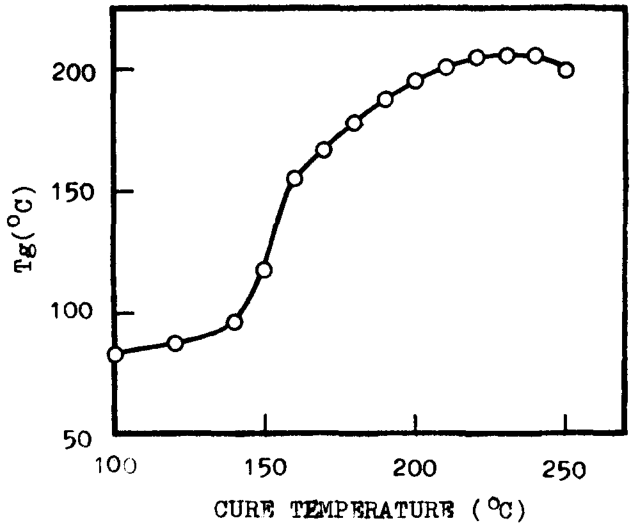

Fig. 4. Glass transition temperature vs. cure temperature for sample 1. Curing time 8 hrs.

It is generally considered that two competing effects are involved in the cure reaction of thermosets. The first is premature quenching as a result of vitrification and the second is depolymerization if the cure temperature is too high. This phenomenon is illustrated in Fig. 4. The figure shows the attained glass transition temperature (Tg) for sample 1 as a function of the cure temperature. As expected, in the low temperature region, we observe the manifestation of the self-quenching process; whereas in the high temperature region the depolymerization reaction occurs, resulting in a decrease in the Tg value.

Fig. 5 shows the glass transition temperature of fully crosslinked E-PEK/DDE system (Tgoo) as a function of the initial molecular weight of the oligomer. For all samples except sample 6, the higher the initial molecular weight, the lower the fully crosslinked glass transition temperature, in agreement with the results in literature on the other oligomers end-capped by groups (14-17). For molecular weight ($\overline{Mn}$) varying between 1,200-4,500, the Tgoo varies between 206-183°C as a result of decreasing crosslinked density. The Tgoo of sample 6 (215°C) is nearly the same as the initial glass transition temperature (214°C) owing to the very low crosslinked density. The Tgoo value for all samples is in the range of 183-215°C and lower than the glass transition temperature of PEK-C resin (228°C).

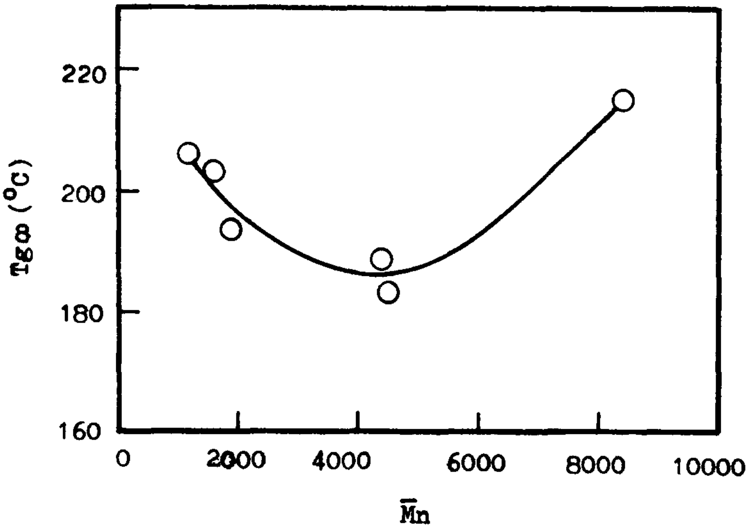

Fig. 5. Tgoo as a function of the initial molecular weight ($\overline{Mn}$) of the oligomer.

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