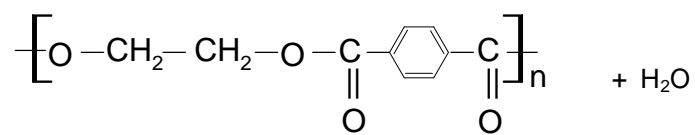
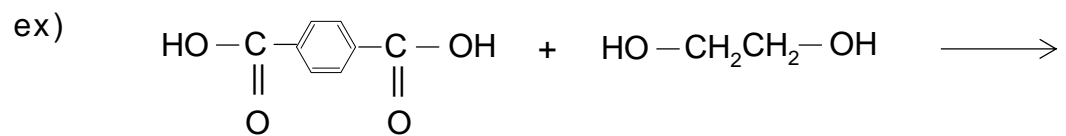


Chapter 2

2.2 Chemistry of Synthesis

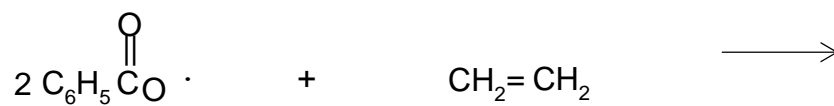
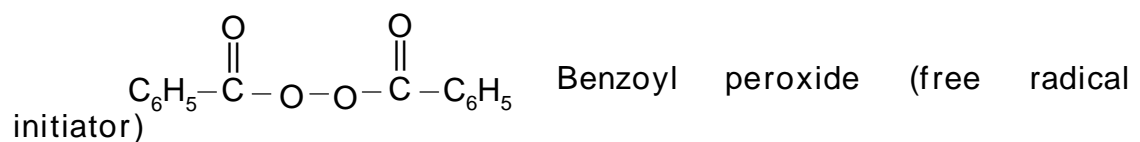
1. Condensation Polymerization (or step-growth)

Diacid + diol \rightarrow polymer

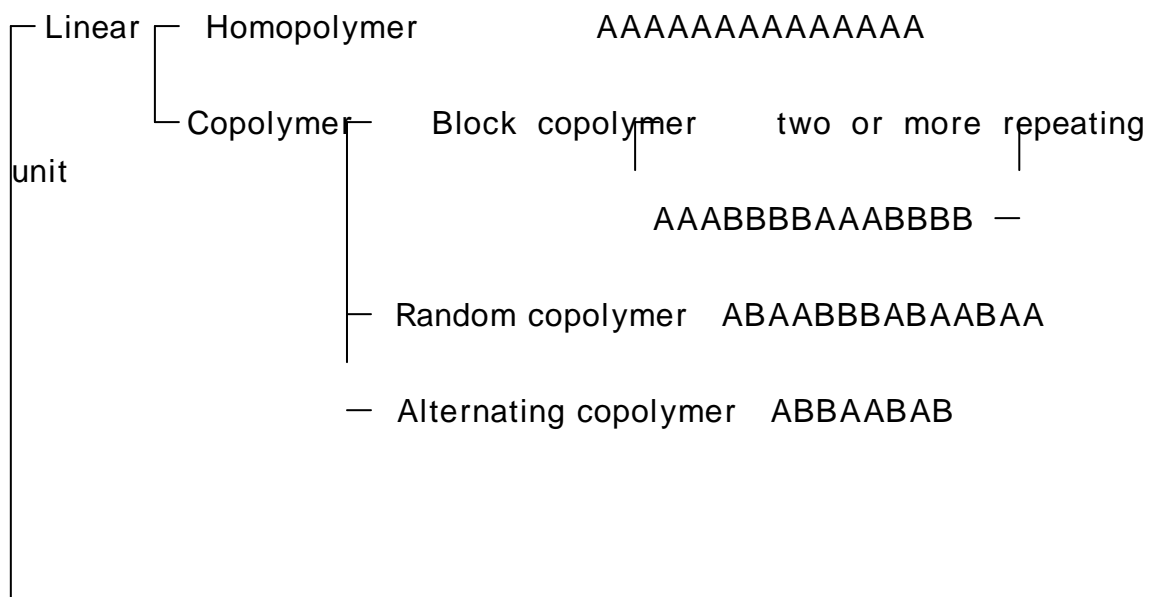


Poly(ethylene terephthalate), PET

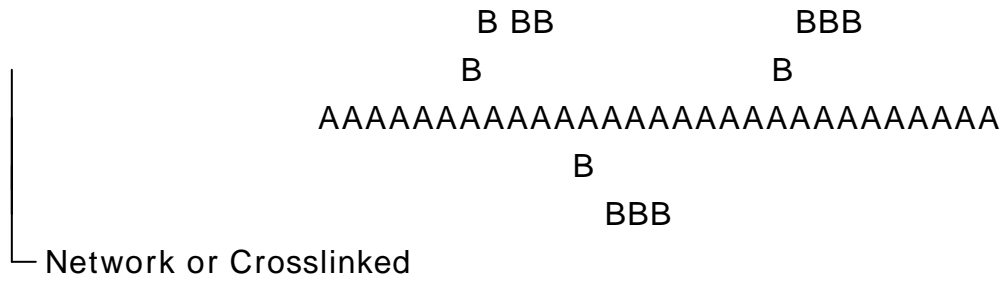
2. Addition Polymerization (chain-growth)



2.3 Structure

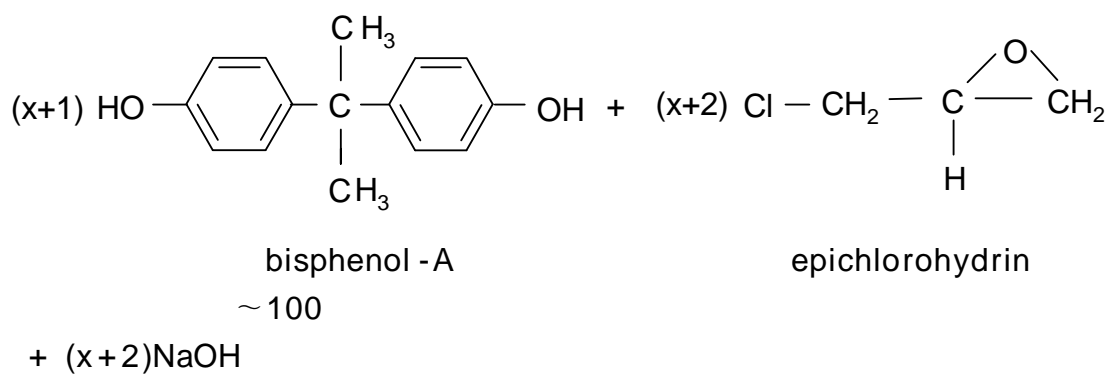


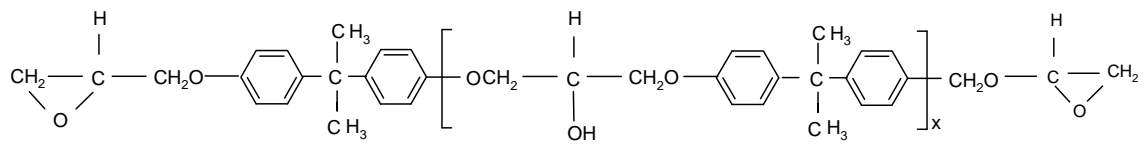
— Branched or Graft copolymer



ex) Random copolymer \rightarrow $\overline{\text{HBA}}$ $\overline{\text{HNA}}$ $\overline{\text{HBA}}$ $\overline{\text{HBA}}$ $\overline{\text{HNA}}$
 graft copolymer \rightarrow HIPS, ABS

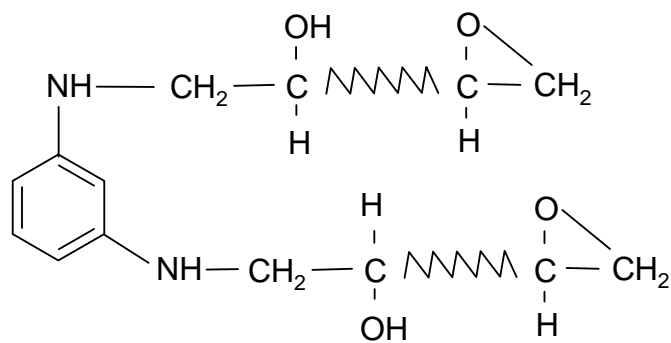
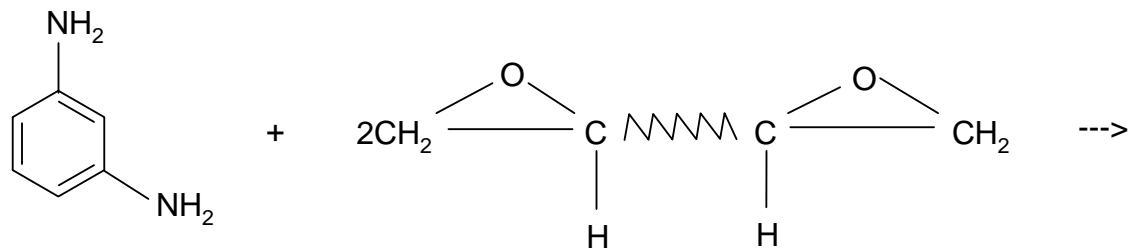
(1) Epoxy





DGEBA(diglycidyl ether of Bisphenol -A)

(2) Curing Rx



Thermal Behavior and Morphology of Rubber-Modified Epoxies

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SYNOPSIS

Rubber-modified epoxies of tetraglycidyl-4,4'-diaminodiphenyl methane and a carboxyl-terminated copolymer of butadiene-acrylonitrile (CTBN) have been investigated by differential scanning calorimetry, scanning electron microscopy, and micrograph image analysis. Bisphenol-A (BPA) was used to produce chain-extended resins by reaction with the epoxy-terminated rubber. Diaminodiphenyl sulfone was used as a hardener. Partially cured resins were prepared with different amounts of added CTBN and cured in an oven for different cure times at 448 K. From the measured heat of reaction of the samples, a fast curing reaction was observed when BPA was present in the resin formulation. In the study of the morphology, the average size of the domains was seen to increase with the CTBN content. These CTBN-rich domains appear to include substantial amounts of epoxy material, as indicated by the measured glass transition temperature of the CTBN-rich phase. The size of domains was observed to range mostly from 0.1 to 5 μm in diameter and to show a slightly bimodal distribution, with modes around 1 μm and 3-4 μm when 15 and 20 phr CTBN was added. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

To improve the impact resistance and fracture toughness of thermoset epoxy resins, low molecular weight liquid rubber-modified epoxies have been studied by many investigators.¹⁻¹² Sultan and McGarry¹ studied rubber-modified epoxies of the diglycidyl ether of bisphenol-A (DGEBA) with a carboxyl-terminated copolymer of butadiene-acrylonitrile (CTBN) and suggested that the observed enhancement in fracture toughness of the rubber-modified epoxy is derived from crazing and band formation. Riew et al.² showed that the addition of bisphenol-A (BPA) to the formulation of the DGEBA/CTBN resin increased the toughening effect of the rubber. In the study of rubber-modified epoxies of DGEBA/CTBN with BPA added to the resin formulation by Manzione et al.,^{5,6} they concluded that the dissolved rubber promotes plastic

deformation and necking at low strain rates, providing large increases in the elongation at break.

For the rubber-modified epoxy resins of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and CTBN,¹³⁻¹⁶ Lee et al.¹³ studied the transition phenomena and the morphology for resins with different amounts of CTBN added. Choe and Oh¹⁶ studied the TGDDM/CTBN blend with the addition of BPA and observed the size of domains using scanning electron microscopy.

Recently, investigators have studied the modification of epoxies with thermoplastics such as poly(ether sulfone)^{17,18} and poly(ether imide)¹⁹ to reduce the lowering of the glass transition temperature while enhancing the fracture toughness of brittle epoxy resins.

In our present study, we examined the thermal behavior of rubber-modified epoxies of the TGDDM/CTBN type with added BPA by determining experimentally the heat of reaction (ΔH) and the glass transition temperature (T_g) by differential scanning calorimetry (DSC). The morphology of the rubber-modified epoxies was examined by

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scanning electron microscopy (SEM) and image analysis of the photomicrographs.

EXPERIMENTAL

Materials

The epoxy resin used in this work was Ciba-Geigy MY720 resin, which consists essentially of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM). The elastomer used as a rubber-modifier was carboxyl-terminated butadiene-acrylonitrile (CTBN) copolymer produced by the B. F. Goodrich Co. under the name of Hycar CTBN 1300 × 13. The characteristics of CTBN are shown in Table I, and the structures of the materials used in this study are shown in Figure 1.

Epoxy and CTBN were prereacted at 353 K in the presence of triphenylphosphine catalyst.¹⁵ Pre-reaction insures the formation of the epoxy-rubber intermediate and promotes blending of the epoxy and the rubber prior to the cure.⁶ Bisphenol-A (BPA) was used to produce chain-extended solid resins by reaction with the epoxy-terminated rubber.^{1,2,6,12,14}

The resin was cured with diaminodiphenyl sulfone (DDS) that was supplied by Ciba-Geigy under the name of hardener HT 976. Methyl ethyl ketone (MEK), 150 parts per hundred resin by weight (phr), was used as a solvent to decrease the viscosity of the resin. The resin formulations with different amounts of CTBN are presented in Table II.

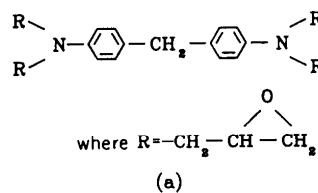
After MEK was eliminated from the resins, partially cured resins were prepared in a vacuum drying oven. For curing, the samples were heated from 298 to 448 K at a heating rate of 2–3 K min⁻¹ in the oven. After reaching 448 K, further curing was conducted in the oven at 30 min increments from 0 to

Table I Characteristics of Carboxyl-terminated Butadiene Acrylonitrile Rubber^a

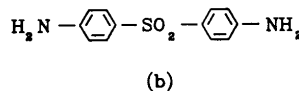
Properties	CTBN (1300 × 13)
Molecular weight	3,500
Acrylonitrile content (wt %)	27
Viscosity, Brookfield, cp (300 K)	570,000
Specific gravity	0.960
Solubility parameter	9.14
T_g^b (K)	215

^a Material and data supplied by B.F. Goodrich Co.

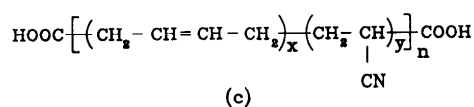
^b Glass transition temperature determined by DSC in our laboratories.



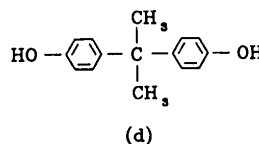
(a)



(b)



(c)



(d)

Figure 1 Molecular structure of the materials used in this study: (a) tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM); (b) diaminodiphenyl sulfone (DDS); (c) carboxyl-terminated copolymers of butadiene-acrylonitrile (CTBN); (d) bisphenol-A (BPA).

300 min. Using the samples prepared according to the above procedure, the morphology of the epoxies was studied.

Differential Scanning Calorimetry

The thermal properties of all samples were measured calorimetrically²⁰ using a Perkin-Elmer differential

Table II Composition of Resins Used in This Study

Chemicals	Resins					
	A	B	C	D	E	F
TGDDM ^a	100	100	100	100	100	100
CTBN (phr) ^b	0	0	5	10	15	20
BPA (phr) ^c	0	24	24	24	24	24
DDS (phr) ^a	52	44	44	44	44	44

^a Supplied by Ciba-Geigy Co.

^b Supplied by B.F. Goodrich Co.

^c Supplied by Junsei Chemical Co.