

# The Kinetics of Polyesterifications. IV. Polyol from BHET and Adipic Acid and its Urethanes

CHEN-CHONG LIN, PING-CHANG YU, and LI-CHAU HUANG,  
*Department of Chemical Engineering, National Taiwan University, Taipei,  
 Taiwan, China*

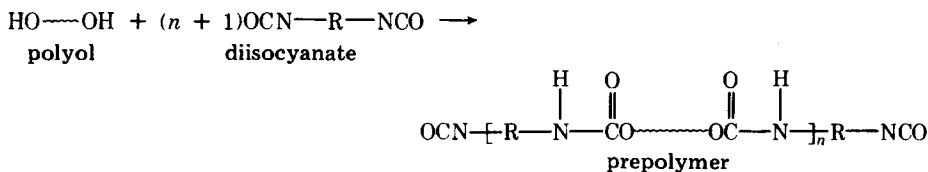
## Synopsis

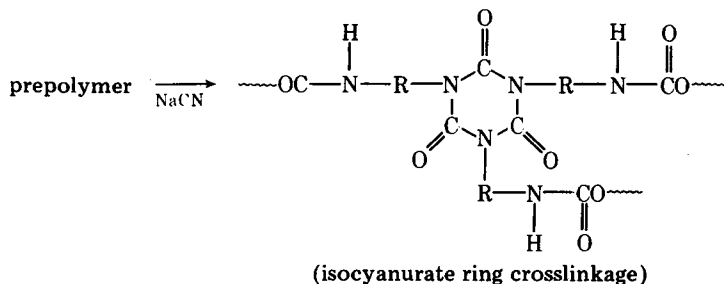
New polyol containing aromatic rings was prepared from BHET, or BHET/ethylene glycol mixtures and adipic acid. In this new system, the kinetics of polyesterification were investigated and were shown to follow the kinetic equations proposed by Lin and his co-workers which were obtained by modifying Flory's theory. Polyurethane elastomers were prepared by reacting these polyols and toluene diisocyanate (TDI) in DMF solution with NaCN as a crosslinking catalyst at room temperature. Their physical properties such as density, gel fraction, swelling ratio, mechanical properties, etc., were measured. High values of elastic modulus are due to the rigid segment of BHET. By varying the molar ratio of diisocyanate and polyester, polyurethanes with different crosslinking densities can be obtained. The relationship between physical properties and crosslinking density was shown to follow the general theory of rubber elasticity.

## INTRODUCTION

The polyester used in polyurethane elastomer has been investigated by many authors. Recently, a new kinetic equation of polyesterifications has been proposed by Lin and his co-workers.<sup>1-3</sup> The mechanism is explained by the dissociation effect of hydrogen ion from dibasic acid in glycol. In order to produce the linear poly(ethylene terephthalate) which is suitable for melt spinning, pure ethylene glycol (EG) is reacted with terephthalic acid, in which bis( $\beta$ -hydroxyethyl terephthalate), BHET, is first produced as an intermediate.

In the present work, BHET and adipic acid or BHET/EG mixtures and adipic acid were chosen as the new systems to further investigate the kinetics of polyesterification. Also, a new type of polyurethane was prepared from these polyesters by reaction with toluene diisocyanate in the presence of a NaCN catalyst to form isocyanurate ring crosslinkage in accordance with Sasaki's method<sup>4,5</sup>:





By varying the ratio of BHET with EG as well as the ratio of TDI with polyester polyol, one can obtain polyurethanes with a wide range of physical properties.

## EXPERIMENTAL

### Materials

Crude BHET produced by esterification of terephthalic acid and EG was reacted with excess EG in autoclave at 240°C and 3 atm for 2 hr, then recrystallized from distilled water to obtain pure BHET; mp = 103–109°C. Adipic acid of reagent grade was recrystallized from conductivity water; mp = 151.5°C. Ethylene glycol, toluene diisocyanate (isomer ratio, 2, 4:2, 6 = 80:20) as well as N,N-dimethylformamide were purified by distillation. Sodium cyanide was pulverized in a mill, dried over silica gel in a desiccator, and then dissolved in DMF by stirring under a stream of nitrogen.

### Apparatus

The apparatus and procedure of polyesterification are the same as employed in our previous paper.<sup>1</sup> Three types of polyester polyol were prepared according to the recipe listed in Table I.

### Preparation of Polyurethane

Polyester polyol was dried under vacuum at 120–150°C with nitrogen sparging before the reaction. Polyester, 6–10 g, was weighed into the reaction bulb and heated to 100°C. Then the polyester was dissolved in 2–6 ml DMF which contained a trace of acid to control the reaction rate. The appropriate molar ratio of TDI was accurately weighed and added into the reaction bulb. Nitrogen was introduced to stir the reaction mixture and to maintain an inert atmosphere. A small portion of the reaction mixture was removed at appropriate time intervals,

TABLE I  
Preparation of Polyester Polyol

Type	BHET/EG	$r^a$	Acid number	$P$	D.P.	MW
A	50/50	1.278	0.44	0.9988	8.132	1115
B	75/25	1.341	0.99	0.9963	6.713	1110
C	100/0	1.425	0.39	0.9983	5.660	1103

<sup>a</sup>  $[\text{OH}]_0/[\text{COOH}]_0$ .

and the residual isocyanate group was titrated by using the amine-equivalent method<sup>6</sup> in order to check the extent of reaction. When the reaction was completed, an appropriate amount of DMF (6–10 ml) was added and the solution cooled down to room temperature. The catalyst solution (0.1 g NaCN/100 ml DMF) was added dropwise, then the reaction bulb was evacuated to eliminate bubbles, and finally the solution was poured into the mold in a desiccator. Gelation took place in a few minutes to a few hours depending on the concentration of prepolymer, the concentration of catalyst, and the environmental temperature. The molded material was left standing overnight and then was dried at 50°C under vacuum to produce three-dimensional polyurethane. The recipes for the different products produced are listed in Table II.

### Measurements

The densities of the produced elastomers were determined with a pycnometer. Gel fraction and swelling ratio were measured by immersing a piece of polyurethane in benzene. The sol fraction dissolved in benzene while the gel fraction swelled. The gel fraction  $g$  and the swelling ratio  $q$  were obtained by using Sasaki's equation.<sup>5</sup> Stress-strain curves were determined by using a Instron tester with 500 mm/min extension rate at room temperature. The initial tangent modulus was measured by a 5 mm/min extension rate at room temperature, according to JIS K6301. Hardness was measured by a JIS hardness tester in which soft to hard ranges from 0 to 100. The flow initiation temperature was measured by a Koka flow tester (Shimadzu). The operation was performed using the constant-temperature elevation method.

### Calculations

By varying the [NCO]/[OH] ratio one can obtain prepolymers with different molecular weights and thus produce different crosslinking densities in the polyurethane network. The crosslinking density or the density of the elastically effective number of chain elements,  $\nu_e/V$ , the density of aromatic ring, [Ar]/ $V$ , and the density of urethane groups, [U]/ $V$ , can be calculated from the relationships presented by Sasaki<sup>5</sup>:

$$\nu_e/V = 2\nu_0(k - 1)/3V \quad (1)$$

$$[\text{Ar}]/V = (\nu_{\text{TDI}} + n\nu_0)/V \quad (2)$$

$$[\text{U}]/V = 2\nu_0/V \quad (3)$$

where  $\nu_0$  and  $\nu_{\text{TDI}}$  are the number of moles of polyester and TDI, respectively;  $V$  is the total volume of the system; and  $n$  is the number of aromatic rings per molecule of polyester.

## RESULTS AND DISCUSSION

Polyesterifications of BHET alone and mixtures of BHET/EG and adipic acid were performed without a foreign catalyst for both equimolar and nonequimolar ratio at 180°C. An example of the kinetic data is shown in Table III for the C

TABLE II  
Preparation of Polyurethane

Run No.	Polyester type <sup>a</sup>	<i>K</i> <sup>b</sup>	Polyester, $\times 10^{-3}$ mole	TDI, $\times 10^{-3}$ mole	Solvent, ml		Catalyst, ml
					Before <sup>c</sup>	After <sup>d</sup>	
1	A	2.0	6.45	12.89	3	6	3
2	A	1.8	6.35	11.43	3	6	3
3	B	2.2	6.88	15.13	3	8	3
4	B	2.0	6.39	12.79	3	10	2
5	B	1.8	5.62	10.12	3	7	2
6	B	1.6	7.19	11.50	4	7	3
7	B	1.4	4.21	5.90	4	6	2
8	C	2.0	3.69	7.37	4	4	2
9	C	1.6	5.54	8.86	4	6	2
10	C	1.4	4.42	6.18	5	6	2

<sup>a</sup> Refer to Table I.

<sup>b</sup> Initial molar ratio of [NCO] to [OH].

<sup>c</sup> Added before prepolymer formation.

<sup>d</sup> Added after prepolymer formation.

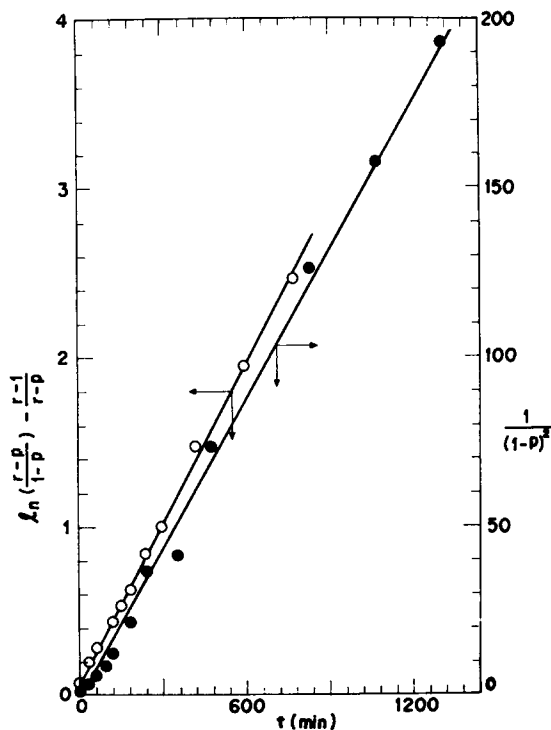


Fig. 1. Kinetic correlation for the uncatalyzed polyesterification of BHET and adipic acid:  $T = 180^{\circ}\text{C}$ ; ( $\bullet$ )  $r = 1.00$ ; ( $\circ$ )  $r = 1.57$ .

TABLE III  
Kinetics of Polyesterification of BHET and Adipic Acid Without Foreign Catalyst<sup>a</sup>

$t$ , min	$c$ , $\frac{\text{equiv. moles}}{\text{kg wet sample}}$	$P$	D.P.	$\ln \left( \frac{r-p}{1-p} \right) - \frac{r-1}{r-p}$
0	3.676	0	1.000	0.087
30	2.079	0.435	1.512	0.193
60	1.667	0.547	1.742	0.255
120	1.017	0.724	2.294	0.442
150	0.833	0.773	2.519	0.537
185	0.694	0.811	2.721	0.635
240	0.487	0.868	3.090	0.851
300	0.355	0.903	3.383	1.071
420	0.211	0.943	3.772	1.476
600	0.121	0.967	4.065	1.956
780	0.069	0.981	4.256	2.470

<sup>a</sup>  $r = [\text{OH}]_0/[\text{COOH}]_0 = 1.57$ ;  $P = ([\text{COOH}]_0 - [\text{COOH}])/[\text{COOH}] = (C_0 - C)/C_0$ ;  $T = 180^{\circ}\text{C}$ .

type polyesterification at  $r = 1.57$ . According to previous studies,<sup>1-3</sup> the plot of  $\ln [(r-p)/(1-p)] - (r-1)/(r-p)$  versus  $t$  for nonequimolar ratio and  $1/(1-p)^2$  versus  $t$  for equimolar ratio should be linear as indicated in Figure 1. As Figure 2 shows, this type of linear relationship was also observed for the BHET/EG and adipic acid systems (types A and B). These correlations prove the validity of Lin's theory for the kinetics of polyesterification.<sup>1-3</sup> Polyesterifications of these three types of polyester, however, did not follow the newly proposed kinetic equation for the case of a catalyzed reaction, since water diffusion controls the reaction rate in these systems which exhibit a high viscosity, even at the early stage of the reactions.

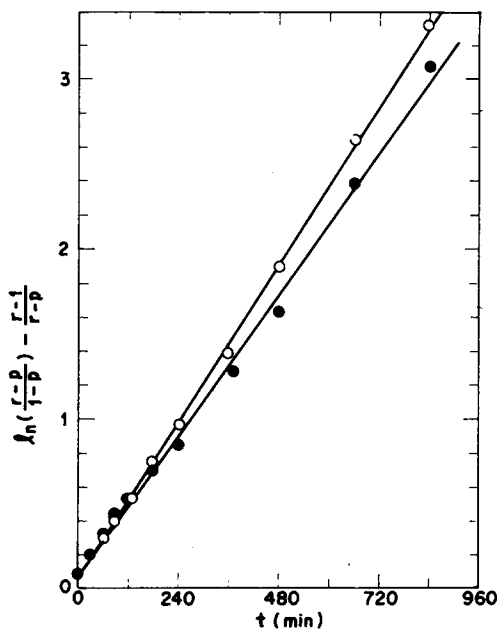


Fig. 2. Kinetic correlation for the uncatalyzed polyesterification BHET, EG, and adipic acid.  $T = 180^{\circ}\text{C}$  (●) BHET: EG = 49:51;  $r = 1.58$ . (○) BHET: EG = 75:25;  $r = 1.57$ .

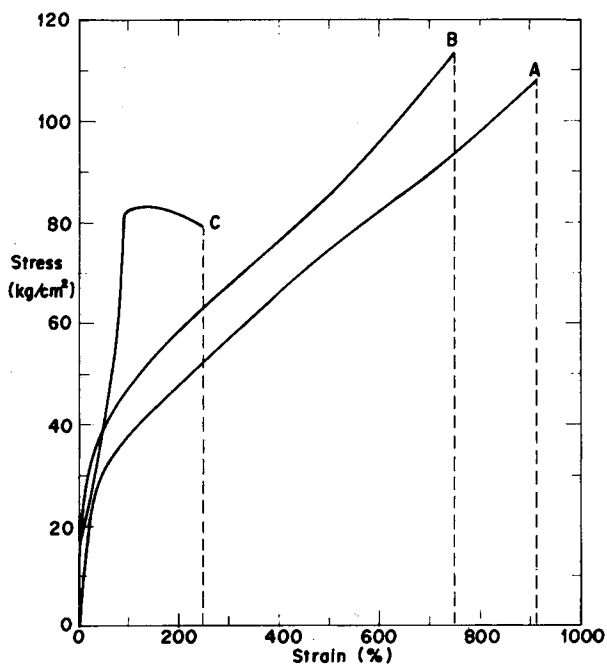


Fig. 3. Stress-strain curves for types A, B, and C polyester-TDI elastomers.

Three types of polyester were synthesized which have an acid number less than 1 and a molecular weight near 1100. Because of the high viscosity of these new systems, it was very difficult or impractical to obtain higher molecular weights of these kinds of polyester. Water is produced as the polyesterification proceeds, but the removal of this water from the system is very difficult. As a result, the

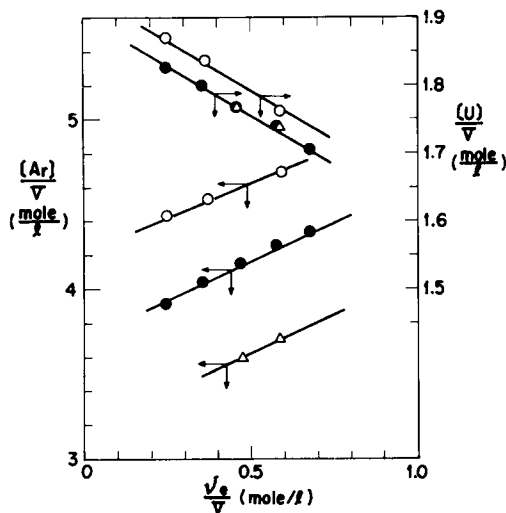


Fig. 4.  $[Ar]/V$  and  $[U]/V$  vs.  $\nu_e/V$  for polyester-TDI elastomers: ( $\Delta$ ) A-type polyester-TDI; ( $\bullet$ ) B-type polyester-TDI; ( $\circ$ ) C-type polyester-TDI.

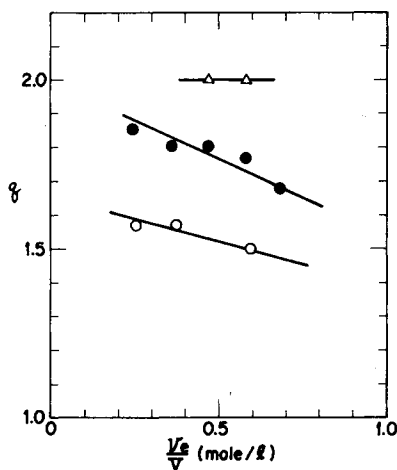


Fig. 5. Swelling ratio vs.  $\nu_e/V$  for polyester-TDI elastomers: ( $\Delta$ ) A-type polyester-TDI; ( $\bullet$ ) B-type polyester-TDI; ( $\circ$ ) C-type polyester-TDI.

water will be accumulated in the system, and the system quickly attains an equilibrium state in which no further reaction occurs.

As shown in Figure 2, ten kinds of polyurethanes with different crosslinking densities were prepared from these three types of polyester. The properties of polyurethanes with  $K = 2$  produced from the different types of polyester are listed in Table IV. Their stress-strain curves are shown in Figure 3. The values listed in Table IV show that the gel fractions are all around 0.9, but B type polyester-TDI exhibits the highest gel fraction, which means it has a more perfect network structure. In the constituents of polyurethane, EG and adipic acid are the soft segments while the aromatic ring, the urethane group, and the isocyanurate ring are the hard segments. The swelling ratio is raised when the soft segment content is raised. High values of the flow initiation temperature as measured by a Koka flow tester mean that the stronger intermolecular force exist in the elastomer (see Table IV).

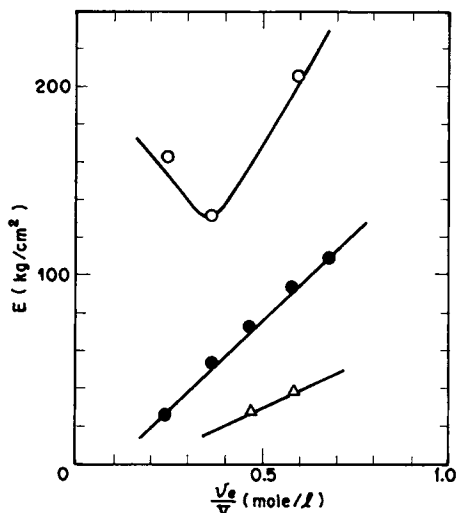


Fig. 6. Elastic modulus vs.  $\nu_e/V$  for polyester-TDI elastomers: ( $\Delta$ ) A-type polyester-TDI; ( $\bullet$ ) B-type polyester-TDI; ( $\circ$ ) C-type polyester-TDI.

Curves A and B in Figure 3 show the normal behavior of an elastomer, even though these materials exhibit higher values of elastic modulus and lower tensile strengths than typical elastomers. The high value of the modulus is attributed to the rigid chain of BHET in the polyurethane, and the lower tensile strength is due to the bulky structure near the crosslinking point, which prohibits crystallization on extension. Curve C in Figure 3 shows both hard and brittle properties as reflected in the relatively high modulus and low value of elongation at break. It tends, however, to be a more brittle material.

The calculated values of  $\nu_e/V$ ,  $[Ar]/V$ , and  $[U]/V$  as well as the physical properties for the ten polyurethane samples are shown in Table IV. The  $[Ar]/V$  and  $[U]/V$  versus  $\nu_e/V$  data of Table IV were plotted to produce Figure 4. These plots show that  $[Ar]/V$  is linearly proportional to  $\nu_e/V$ , while  $[U]/V$  decreases linearly with an increase in  $\nu_e/V$ . The swelling ratios are plotted against  $\nu_e/V$  in Figure 5. This correlation shows that the swelling ratios of both B and C-type polyester-TDI decreases linearly with an increase in  $\nu_e/V$ , while the A-type polyester is not influenced by  $\nu_e/V$ . This means that by decreasing  $\nu_e/V$ , the increase in entropy dominates the contraction force, so that a larger swelling ratio is realized.

Elastic modulus is plotted versus  $\nu_e/V$  in Figure 6. Both the A and B type showed linear relationships for E versus  $\nu_e/V$  as expected from the theory of rubber elasticity; however, the C type elastomer deviates from this idealized elastomer behavior. The variation in the slopes of these plots for each type of polyester-TDI is due to the difference in BHET contents. Tensile strength and elongation at the break point are plotted against  $\nu_e/V$  in Figure 7. Tensile strength increases with increasing  $\nu_e/V$ , and all the data points fall within a band around a single correlation line. Elongation at break decreases with increasing  $\nu_e/V$ . In Figure 8, flow initiation temperatures are essentially independent of  $\nu_e/V$  for A- and C-type elastomers, while for the B type an increase in  $\nu_e/V$  causes an increase in the temperature at which flow begins. This indicates that the intermolecular forces might be increased by increasing  $\nu_e/V$  in the B-type elastomers.



TABLE IV  
 Properties of the Produced Polyurethane

Run No.	Polyester type	$K$	$[U]/V$ , mole/liter	$[Ar]/V$ , mole/liter	$\nu_e/V$ , mole/liter	Density, g/cm <sup>3</sup>	Gel fraction	Swelling ratio	Elastic modulus, kg/cm <sup>2</sup>	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	Hardness	Flow initiation temperature, °C
1	A	2.0	1.735	3.716	0.587	1.270	0.90	2.048	37.30	107.15	913	72	151.6
2	A	1.8	1.768	3.609	0.471	1.263	0.94	2.009	27.15	77.00	1125	58	153.0
3	B	2.2	1.703	4.337	0.681	1.272	0.95	1.674	100.71	111.11	738	80	182.9
4	B	2.0	1.741	4.259	0.580	1.270	0.93	1.764	93.32	109.43	750	78	145.5
5	B	1.8	1.774	4.162	0.473	1.263	0.92	1.799	72.77	65.35	700	74	125.6
6	B	1.6	1.797	4.037	0.359	1.247	0.90	1.793	51.56	58.86	755	72	112.6
7	B	1.4	1.824	3.914	0.243	1.235	0.88	1.845	24.90	57.60	920	66	94.5
8	C	2.0	1.759	4.688	0.586	1.277	0.90	1.497	205.18	82.68	250	82	109.0
9	C	1.6	1.839	4.534	0.368	1.271	0.89	1.574	128.72	67.12	325	80	100.9
10	C	1.4	1.869	4.420	0.249	1.259	0.90	1.559	163.20	64.66	663	79	110.4

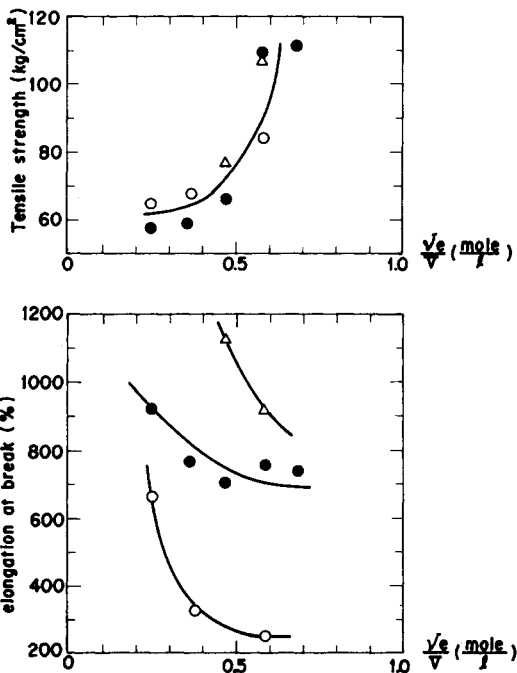


Fig. 7. Tensile strength and elongation at break vs.  $\nu_e/V$  for polyester-TDI elastomers: ( $\Delta$ ) A-type polyester-TDI; ( $\bullet$ ) B-type polyester-TDI; ( $\circ$ ) C-type polyester-TDI.

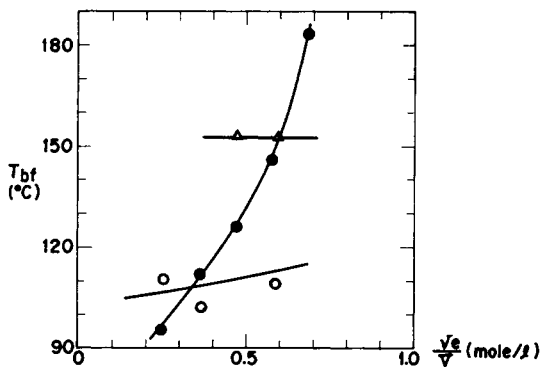


Fig. 8. Flow initiation temperature vs.  $\nu_e/V$  for elastomers: ( $\Delta$ ) A-type polyester-TDI; ( $\bullet$ ) B-type polyester-TDI; ( $\circ$ ) C-type polyester-TDI.

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