# Preparation and Properties of Polyester–Urethane Block Copolymers

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#### **INTRODUCTION**

The research to be described was initiated in 1955 as a study of linear block polymer synthesis by means of polyaddition reactions. In a previous paper<sup>1</sup> we have reported on the polyaddition reaction of bis(hydroxypolyoxyethylene) terephthalate,

 $HO(CH_2CH_2O)_nCO$   $-CO(OCH_2CH_2)_nOH$ 

and diisocyanate that yields linear elastic polyurethanes. The elasticity of the polymers may be due to the "fitting effect"<sup>2,3</sup> of the terephthaloyl group, which is arranged regularly in the polymer chain; this effect is the same as that of crosslinking. Snyder<sup>4</sup> prepared an elastic, linear copolyester of dimethyl terephthalate, dimethyl sebacate, and ethylene glycol; Edgar and Hill<sup>5</sup> reported on polyethylene terephthalate adipate and polyethylene terephthalate sebacate copolyesters, both of which show a minimum in the melting point-composition curve. This curve may be expressed by the following equation proposed by Flory:<sup>6,7</sup>

$$(1/T_m) - (1/T_m^{\circ}) = (-R/H_u) \ln X_A \qquad (1)$$

where  $T_m$  and  $T_m^{\circ}$  are the melting points of the copolymer and homopolymer, respectively,  $H_u$  is the latent heat of fusion of the homopolymer, and  $X_A$  is the molar fraction of major component A. In contrast, the melting point of the crystalline block copolymer does not decrease with molar fraction but depends only on the average length of the block of crystallizing units.<sup>8</sup> This dependence bears a similarity to the relation of the melting point to the molecular weight of a polymer, expressed by an equation owed to Evans, Mighton and Flory:<sup>7</sup>

$$(1/T_m) - (1/T_m^{\circ}) = 2R/(H_u \bar{X}_n)$$
(2)

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† Present address: Teijin Chemical Industries Co., Matsuyama, Ehime-ken, Japan. where  $T_m^{\circ}$  is the melting point of a polymer of extremely high molecular weight, and  $\bar{X}_n$  is the number-average degree of polymerization.

Coleman,<sup>9</sup> and Charch and Shivers<sup>10</sup> prepared a block copolymer of ethylene terephthalate and polyethylene glycol:



and found that the melting point depression follows Flory's eq. (1), in compliance with the amount of polyethylene glycol. This may be understood by noting that the size of the ethylene terephthalate block, i.e., the magnitude of m in the above formula, varies inversely with the molar fraction of polyethylene glycol. If block copolymers can be prepared under conditions such that the average length of each type of block does not vary with the molar fraction, then the melting points will change little with composition in most cases.

Since diisocyanate is highly reactive toward polymer fragments with hydroxyl endgroups, it is easy to obtain a block copolymer in which the average lengths of the block species do not vary with molar fraction.

In this paper we describe the synthesis of polyester-urethane block copolymers from diisocyanate and polyester with polyethylene terephthalate as one block, and give the melting points, second-order transition temperatures, and some other physical properties of these copolymers.

#### EXPERIMENTAL

Block copolymers were prepared by the polyaddition reaction of diisocyanate with polyesters formed by the condensation of glycol and dicarboxylic acids. The polyesters used were polyethylene terephthalate (PET) and either polyethylene succinate (PESu), polyethylene adipate. (PEA), polydiethylene adipate (PDA), polyethylene azelate (PEAz), polyethylene sebacate (PES), polyethylene phthalate (PEP), or polyethylene iso-

#### **Preparation of Polyethylene Terephthalate**

phthalate (PEI).

In a 500-ml. flask provided with a stirrer, an inlet tube for nitrogen, and a short, packed column leading to a condenser and receiver, 197 g. (1 mole) of dimethyl terephthalate and 155 g. (2.5 moles) of ethylene glycol were heated in the presence of small amounts of zinc acetate as catalyst at 200°C. for 3 hr. During the reaction, methanol was distilled off. The reaction mixture was then heated under 0.2-0.3 mm. at 285°C. for 5 hr. to distill off ethylene glycol. Stirring was effected by periodically introducing a current of nitrogen through the reaction mass.

# **Preparation of Other Polyesters**

In the same apparatus, 1 mole of dibasic acid and 2.5 moles of ethylene glycol or diethylene glycol were heated at 180–200 °C. for about 3 hr., and under 0.2–0.3 mm. at 200 °C., until the reaction product attained a molecular weight of about 2000–3000.

### **Molecular Weights of the Polyesters**

The molecular weights of the polyesters were calculated from the results of endgroup analysis. Polyethylene terephthalate was titrated according to Pohl's method<sup>11</sup> after the hydroxyl endgroups were converted to carboxyl groups by reaction with succinic anhydride.<sup>12,13</sup> The hydroxyl endgroups of low-melting polyesters were determined through acetylation by pyridine-acetic anhydride reagent,<sup>14,15</sup> and the carboxyl endgroups were titrated directly in acetone solution with 0.01N alcoholic KOH.

 TABLE I

 Melting Points and Molecular Weights of Polyesters

Polyester	Melting point, °C.	$\begin{array}{l}\text{COOH} \\ \text{content,} \\ \text{equiv./g.} \\ \times 10^6 \end{array}$	$\begin{array}{c}\text{OH} \\ \text{content,} \\ \text{equiv./g.} \\ \times 10^{\circ} \end{array}$	$egin{array}{c} \mathbf{Molecular} \ \mathbf{weight} \ \overline{M}_n \end{array}$
PET	250-255	4.5	688	2890
PESu	94 - 95	8.1	785	2520
PEA	53 - 55	7.4	709	2970
PDA	Oily	8.5	1154	1720
PEAz	45-46		597	3350
PES	74-75	7.0	750	2640
PEP	Glassy	9.8	807	2450
PEI	110-115	6.8	792	2500

The melting points and molecular weights of the polyesters prepared are shown in Table I.

### Diisocyanate

Tetramethylene diisocyanate was prepared from adipoyl dihydrazide and sodium nitrite through a Curtius rearrangement:<sup>16</sup>

$$\begin{array}{cccc} H_2NNHC(CH_2)_4CNHNH_2 & \xrightarrow{NaNO_2, HCl} \\ & \parallel & & \parallel \\ O & O \\ & & &$$

Into 1000 ml. of an aqueous solution kept at 0°C. containing 174 g. (1.0 mole) of adipovl dihydrazide and 210 g. (2.0 moles) of 35% hydrochloric acid, 140 g. (2.0 moles) of sodium nitrite in 150 ml. of water was added dropwise with stirring. An exothermic reaction occurred immediately, and as soon as the temperature rose above 5°C., 500 ml. of benzene was added. The reaction was continued at 5-8°C. for 30-40 min. The reaction mixture was then filtered and the benzene layer separated from the aqueous phase. The aqueous solution was extracted twice, each time with 200 ml. of benzene. The benzene solutions were combined and, after being dried over calcium chloride for half an hour. were heated gradually with cautious stirring in a 2-1. three-necked flask. A vigorous exothermic decomposition occurred at 40-60°C., lasting for 70 After removal of solvent under reduced min. pressure, the product was distilled at 112-113°C. (20 mm.). The yield was 91-101 g. (65-72%).

#### **Block Polyaddition Reaction**

When two polyesters are mixed together at an elevated temperature, an ester interchange reaction can occur producing a haphazard arrangement of the two repeating units, i.e., a random copolymer. However, it was found little ester interchange occurred when the polyaddition reaction of polyesters with diisocyanate was carried out in nitrobenzene solution at  $170^{\circ}$ C.

For example, in a 200-ml. three-necked flask provided with a stirrer, a  $CaCl_2$  tube, and a thermometer, 3.3 g. (1.14 mmoles) of polyethylene terephthalate and 16.7 g. (5.59 mmoles) of polyethylene adipate were dissolved in 30 ml. of nitrobenzene at 170°C. Tetramethylene diisocyanate (1.00 g.; 7.13 mmoles) was added to the solution and the mixture was heated with stirring at 170°C. for 3 hr. The solution was then poured into 500 ml. of

	Polyesters		Totramothylana					
	Ethylene	A = PET		diisocyanate.			Melting	
	terephthalate.	moles	B. moles	moles	Nitrobenzene,	Yield,	point,	[n]
Sample	mole-%	$ imes 10^{-3}$	$\times$ 10 <sup>-3</sup>	$ imes 10^{-3}$	ml.	%	ΰC. ́	(30°C. in m-cresol)
T 100	100	6.92	0	6.92	160	94.5	245-250	0.42
B = PESu								2
Su 100	0	0	10.0	10.0	0	100.0	98-110	0.50
Su 90	10	0.796	7.02	7.82	<b>20</b>	92.3	98-110	0.54
Su 85	15	1.59	6.11	7.70	40	92.5	150 - 200	0.48
Su 65	35	2.70	4.84	7.54	70	92.3	240 - 243	0.46
Su 50	50	3.94	3.41	7.35	100	92.8	245 - 250	0.38
Su 35	65	4.91	2.30	7.21	120	93.4	245 - 250	0.40
Su 15	85	6.12	0.913	7.03	140	94.4	245 - 250	0.40
$\mathbf{B} = \mathbf{PEA}$								
A 100	0	0	10.0	10.0	0	100.0	45 - 46	0.50
A 95	5	0.381	6.77	7.15	20	90.2	45 - 46	0.48
A 90	10	0.761	6.38	7.14	20	92.9	120 - 160	0.45
A 85	15	1.14	5.99	7.13	30	92.9	207 - 214	0.42
A 65	35	2.60	4.48	7.08	60	93.5	247 - 252	0.44
A 50	50	3.65	3.39	7.04	90	94.5	247 - 252	0.44
A 35	65	4.67	2.33	7.00	110	94.3	247 - 252	0.43
A 15	85	5.92	1.04	6.96	140	94.3	247 - 252	0.41
$\mathbf{B} = \mathbf{PDA}$								
DA 100	0	0	11.6	11.6	0	100.0		0.65
DA 95	5	0.311	11.1	11.4	20	88.9		0.63
DA 90	10	0.622	10.6	11.2	20	90.3	140-160	0.59
DA 85	15	0.934	10.1	11.0	25	92.2	170-210	0.59
DA 65	35	2.25	7.95	10.1	55	94.5	240-245	0.48
DA 50	50	3.25	6.16	9.41	80	93.2	245-250	0.47
DA 35	65 <sup>.</sup>	4.01	4.88	8.89	100	94.0	245-250	0.45
DA 15	85	5.78	1.92	7.70	140	94.0	245 - 250	0.42
$\mathbf{B} = \mathbf{PEAz}$	2	0	<b>x</b>	0.00	20	00 <b>F</b>		1 10
Az 100	0	0	5.98	6.00	20	92.5	45-48	1.19
Az 95	5	0.281	5.70	6.10	25	99.5	45-48	0.96
Az 90	10	0.566	5.45	6.10 6.10	25	95.0	195-199	0.83
Az 85	15	0.855	<b>5.15</b>	6.10	30	93.0	230-234	0.99
Az 65	30 50	2.04	4.03	0.10	00	90.0	249-200	0.74
Az 50	50 75	4.81	5.15 1.61	0.10	80 190	90.0	249-200	0.34
AZ ZƏ D DES	(5	4.07	1.01	0.21	120	91.5	240-200	0.04
B = PES	0	0	10.0	10.0	0	100.0	60-72	0.55
5 100	10	0 657	7 26	10.0	20	02.3	70-76	0.55
5 90 S 95	10	0.007	7.07	7 07	20	02.5 02.6	105-200	0.55
5 65 S 65	15	9 15	5 61	7 76	20 50	02.0	230-235	0.51
S 60	50	2.10	4 30	7.57	80	04 N	200 200	0.48
S 35	65	3 04	3 50	7 44	100	94 0	245-250	0.45
S 15	85	5 71	1 42	7.13	140	95.1	245 - 250	0.42
B = PEP	00	0.11		1120		00.2	210 200	
P 100	0	0	10.0	10.0	0	100.0		0.52
P 90	10	0.692	7.35	8.04	20	90.2	150-170	0.48
P 85	15	1.04	6.94	7.98	30	92.1	195-200	0.47
P 65	35	2.42	5.31	7.73	60	92.3	235-240	0.47
P 50	50	3.46	4.08	7.54	80	94.5	245-250	0.45
P 35	65	4.50	2.86	7.36	105	94.5	245 - 250	0.44
P 15	85	5.88	1.22	7.10	140	95.0	245-250	0.41
B = PEI		-		-				
I 100	0	0	10.0	10.0	0	100.0	98-105	0.52
I 95	5	0.346	7.60	7.95	20	86.1	98-104	0.50
1 90	10	0.692	7.20	7.89	20	89.3	98-104	0.50
I 85	15	1.04	6.80	7.84	30	91.2	190200	0.47
I 65	35	2.42	5.20	7.62	60	94.3	245 - 250	0.45
I 50	50	3.46	4.00	7.46	80	94.0	245 - 250	0.45
I 35	65	4.50	2.80	7.30	105	94.0	245 - 250	0.44
I 15	85	5.88	1.20	7.08	140	94.0	245 - 250	0.43
<u></u>					·····			

TABLE II. Preparation, Melting Points, and Intrinsic Viscosities of Polyester-Urethane Block Copolymers

methanol and a white, rubberlike polymer was obtained, which after being washed with 300 ml. of boiling methanol three times was dried in a vacuum desiccator. The yield of block copolymer was 19.5 g. (92.9%).

# Melting Points and Second-Order Transition Temperatures

Samples for the melting point and second-order transition temperature determinations were annealed to crystallize at 150°C. for 3 hr.

Measurements of the melting points were made with the use of a hot-stage microscope.

The second-order transition temperatures were measured in a dilatometer with a capillary 2 mm. in diameter and 50 cm. long, as described by Bekkedahl.<sup>17</sup> All samples were measured over the range of -30 to +120°C., except for samples A65, A85, Az65, and Az85 (Tables II and IV), which were examined from -70 to +80°C.

TABLE III Solubilities of Polyester–Urethane Block Copolymers<sup>6</sup>

Ethyl-	Solubility of copolymer						
tere- phthal- ate, mole-%	Phenol, cresol	Nitro- ben- zene	Di- oxane	Ace- tone	Ben- zene	Etha- nol, metha- nol	
0	++	++	++	++	++	_	
5	++	++	++	++	+	-	
10	++	++	+	±	±	-	
15	++	+	+	±	Ŧ	-	
35	++	+	+	±	±	-	
50	++	+	±	±	±	-	
65	++	+	±	±	±	-	
85	++	+	±	±	±		
100	+	+	±	-	_	-	

\* Here (++) denotes soluble at room temperature; (+) soluble with heating; (±) insoluble but swollen; (-) insoluble.

# Miscellaneous Measurements on the Polyester--Urethane Block Copolymers

In attempts to assess the effects on physical properties of modifying the chain structure of a block copolymer, it is important that the molecular weights of all the experimental block copolymers be of the same order. To check this, the intrinsic viscosities of the polymers, were measured in *m*cresol at  $30^{\circ}$ C.

X-ray diffraction measurements were performed at the Laboratory of X-ray Analysis of the Tokyo Institute of Technology. Samples were unstretched, plane films 0.2 mm. thick, which were annealed at 150°C. for 10 hr.

# **RESULTS AND DISCUSSION**

The preparation, melting points, and intrinsic viscosities of the polyester-urethane block copolymers are shown in Table II.

In the block copolymers prepared by us, the blocks could be randomly arranged, since all four hydroxyl endgroups of the two polyesters were expected to be equally reactive to diisocyanate. For example, if we denote

$$-OCH_2CH_2O-[-CO-COOCH_2CH_2O-]_x$$
  
 $-CONH(CH_2)_4NHCO-$ 

by -B-, where x and y are integral numbers on the order of 10-20, then we can express the structure of a block copolymer composed 20% of Ablocks by

B-B-B-A-B, B-A-B-A-B-B-B-B-B, or B-B-B-A-B-B-B-B-A-B-B, etc.

# **Crystalline Regions of the Block Copolymers**

In Figure 1 are shown the melting point-composition curves for the block copolymers. These step-shaped curves are characteristic of crystalline block copolymers. The location of the abrupt



Fig. 1. Melting point vs. composition of polyester-urethane copolymers: (1) PET/PESu, (2) PET/PEA, (3) PET/PDA, (4) PET/PEAz, (5) PET/PES, (6) PET/PEP, (7) PET/PEI.



Fig. 2. X-ray diffraction diagrams of polyester-urethane block copolymers.

change of the melting point with composition probably depends upon the crystallinity of the two components. X-ray diffraction diagrams of PET/ PEA and PET/PEP block copolymers, shown in Figure 2, indicate that the crystallites of the block copolymers are identical with those of the pure



Fig. 3. Depression from 250°C. of melting point of 50/50 PET/PEA-urethane block copolymer.

Copolymers (Regulta of unburge dilatometry)							
(Results of volume dilatometry)							
	DEVE	First-order	Second-order				
	PEI	tomporeture	tomporature				
G	content,	emperature,	vernperature,				
Sample	wt%	<u> </u>					
$\mathbf{PET}$	100	_	80ª				
Su 15	88.5	_	71				
Su 35	71.0	95 <sup>b</sup>	47				
Su 50	57.0	95 <sup>b</sup>	0f 36.5				
Su 65	41.7	100 <sup>b</sup>	$-1^{f}$ 27				
Su 90	12.9	105	5				
PESu	0	106	$-1^{f}$				
A 15	85.5		42, 68				
A 35	67.5		0,68				
A 50	52.8	44 <sup>b</sup>	-20				
A 65°	37.5	<b>46</b> <sup>b</sup>	-41				
A 85°	16.5	<b>46</b> <sup>b</sup>	-60				
PEA <sup>o</sup>	0	53	$-70^{d}$				
Az 25	73.0	44 <sup>b</sup>	27				
Az 50	47.3	44 <sup>b</sup>	- 6				
Az 65°	32.6	44 <sup>b</sup>	-30				
Az 85°	13.7	44 <sup>b</sup>	-34				
Az 90°	9.05	41 <sup>b</sup>	-39				
PEAz <sup>o</sup>	0	41	-45				
S 15	82.5		50, 68				
S 35	57.0		18				
S 50	46.0	70 <sup>b</sup>	0				
S 65	31.0	72 <sup>b</sup>	-15				
S 85	13.0	74 <sup>b</sup>	-24				
PES	0	78	-30				
P 15	85		46, 68				
P 35	65	<u> </u>	29				
P 50	50		<b>24</b>				
P 65	35	—	22				
P 85	15	<u> </u>	18				
PEP	0	_	17				
I 15	85		43, 73				
I 35	65		36,72.5				
I 50	50		35				
I 65	35		30				
I 85	15	—	26				
PEI	0	<u> </u>	24°				

TABLE IV Transition Temperatures of Polyesters-Urethane Block

\* Reference 18: 81°C. (cryst.), 69°C. (amorph.).

<sup>b</sup> Transition could not be observed with the hot-stage microscope.

° Sample was examined from -70 to +80 °C.

<sup>d</sup> Reference 5: -70 °C.

<sup>e</sup> Reference 18: 51°C. (amorph.).

<sup>f</sup> Transition temperatures due to PESU segments.

homopolymer, and that crystallites of both components are present in most compositions of the block copolymers. Dilatometric measurements of the block copolymers showed definite first-order transition points at the melting points of PESu, PEA, PEAz, or PES, indicating their presence in crystallite form, although no deformation points were observed through the hot-stage microscope. For the melt blends of two polyesters two deformation points were observed through the hot-stage microscope, owing to the fact that crystallites of both components were formed in all compositions.<sup>7</sup> In PET/PEP and PET/PEI block copolymers, however, it was proved by the results of x-ray diffraction and volume dilatometry that only one type of crystallite (that of PET) was present, indicating that PEP or PEI segments are located in the amorphous regions.

Like the polyester melt blends, polyester-urethane block copolymers are change into random copolymers by heating. Figure 3 shows the melting point depression curve for a PET/PEA-50/50 urethane block copolymer after it had been kept at 250°C.

PET is soluble in phenol, cresol, and hot nitrobenzene and swells in dioxane but is insoluble in benzene, acetone, and alcohols. On the other hand, the low-melting polyesters used as block components are soluble in benzene, dioxane, and acetone. The solubilities of the block copolymers in these solvents are shown in Table III. A block copolymer containing less than 5% of polyethylene terephthalate is also soluble in benzene and acetone, just as are the low-melting polyesters. This indicates that polyethylene terephthalate does not crystallize if it is present in concentrations less than 5 mole-%. This has been shown also by the melting-point behavior of block copolymers. Other block copolymers swell in acetone and benzene but do not dissolve even when heated. The swollen polymer probably includes the insoluble crystallites of polyethylene terephthalate.

### **Amorphous Regions of the Block Copolymers**

The relation between the second-order transition temperatures and the composition of block copolymers is not known. For random copolymers, Gordon and Taylor<sup>19</sup> derived the relation

$$W_{2} = (T_{g} - T_{g_{1}})/k[(T_{g_{2}} - T_{g}) + (T_{g} - T_{g_{1}})] \quad (3)$$
$$k = \Delta\beta_{2}/\Delta\beta_{1}$$

and  $T_{\varrho}$ ,  $T_{\varrho_1}$ , and  $T_{\varrho_2}$  are, respectively, the secondorder transition temperatures of the copolymer and of the homopolymers 1 and 2,  $W_2$  is the weight fraction of component 2, and  $\Delta\beta$  is the difference between the thermal expansion coefficient, above and below the transition temperature.

The transition temperatures of polyesterurethane block copolymers measured by volume dilatometry are listed in Table IV. It is interesting to note that some block copolymers have two second-order transition temperatures, one of which may be comparable to that of the pure major component.

The differences between the thermal expansion coefficients above and below the transition temperature  $\Delta\beta$ , obtained by volume dilatometry, are summarized in Table V.

TABLE V Thermal Expansion Coefficients of Polyesters Above and Below  $T_a$ 

Polyester	Thermal e			
	Above $T_g$ , deg. <sup>-1</sup> $\times 10^5$	Below $T_g$ , deg. <sup>-1</sup> $\times 10^5$	$\begin{array}{c} \Delta\beta, \\ \mathrm{deg.}^{-1} \\ \times 10^{5} \end{array}$	Ratio kª
PET	29.17	22.28	6.89	1
PESu	40.35	31.58	9.27	1.35
PES	35.8	19.6	16.2	2.35
$\mathbf{PEP}$	59.32	17.42	41.90	6.08
PEI	53.16	19.96	33.20	4.82

<sup>a</sup> Ratio of  $\Delta\beta_2$  (polyester) to  $\Delta\beta_1$  (PET).

In Figure 4 are shown the second-order transition point-composition data for the block copolymers, together with curves calculated from eq. (3) by use of the values of k in Table V. Within experimental error, the experimental second-order transition



Fig. 4. Second-order transition point vs. composition of polyester-urethane block copolymers.

ephthalate (ET)							
Polyester–urethane block copolymers	15 mole-% ET		35 mole-% ET		50 mole-% ET		
	Tensile strength, kg./cm. <sup>2</sup>	Elongation, $\%$	Tensile strength, kg./cm. <sup>2</sup>	Elongation, %	Tensile strength, kg./cm. <sup>2</sup>	Elongation %	
PET/PESu	110	6.7	3	<u></u> 8	8,	8	
PET/PEA	240	700	285	500	372	100	
PET/PDA	120	200	134	113	282	90	

90

169

400

TABLE VI Stress-Elongation Data for the Polyester-Urethane Block Copolymers Containing Various Proportions of Ethylene Terephthalate (ET)

<sup>a</sup> Too brittle to test.

PET/PEAz

PET/PES

point-composition curves are identical with those calculated from eq. (3).

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#### **Elastic Properties of the Block Copolymers**

Table VI lists tensile strength and elongation data for dumbbell-shaped samples of block copolymers tested at 20°C. The samples with second-order transition temperatures higher than 20°C. were too brittle to be tested for elongation, but they became elastic when heated. S 85 and diisocyanate extended linear polyesters are hard and waxy despite their low second-order transition temperatures, owing to their high degree of crystallinity.

The samples listed in Table VI were found to be elastic, the PET/PEA block copolymers being the best in this respect. This may be accounted for by assuming that crystallites of polyethylene terephthalate were joined to the flexible polymer chain in the amorphous region, so that a type of network structure similar to crosslinking was formed.

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# **Synopsis**

Polyester-urethane block copolymers were prepared by the block polvaddition reaction of diisocvanate with two kinds of linear polyesters, one of which was polyethylene terephthalate. The melting points of polyester-urethane block copolymers containing more than 30% polyethylene terephthalate are independent of the total molar fraction of the two polyester components, so that the melting pointcomposition curves are step-shaped. The relation between the second-order transition point of the block copolymer and its composition, on the other hand, is the same as that for a random copolymer. It is observed that some polyesterurethane block copolymers containing 15-50% of polyethylene terephthalate have elastic properties. For example, the 15/85 polyethylene terephthalate/polyethylene adipate-tetramethylene diisocyanate block copolymer has a tensile strength of 240 kg./cm.<sup>2</sup> and an elongation of 700%. It may be supposed that these elastic properties are due to the structure of the block copolymer chains: the flexible polymer chains in the amorphous region may be joined to the crystallites of polyethylene terephthalate, so that a type of network structure similar to crosslinking is formed.

#### Résumé

On a préparé des copolymères à blocs polyester-uréthanne par réaction d'un diisocyanate avec deux polyesters linéaires dont l'un était Ie téréphthalate de polyéthylène. Les points de fusion des copolymères contenant plus de 30% du

téréphtalate de polyéthylène sont indépendants des fractions molaires des deux composants polyesters; les courbes des points de fusion en fonction de compositions montent progressivement. La relation entre les points de transition de second ordre de copolymères à blocs et leurs compositions est la même que celle obtenue dans le cas des copolymères statistiques. On observe que quelques copolymères à blocs polyester-uréthanne contenant de 15 à 50% du téréphtalate de polyéthylène ont des propriétés élastiques caoutchouteuses. Par exemple, le copolymère à blocs de téréphtalate de polyéthylène et d'adipate de polyéthylène (15: 85)/diisocyanate de tétraméthylène a une résistance à la traction de 240 kg/cm<sup>2</sup> et une élongation de 700%. On peut considérer que les propriétés élastiques sont dues à la structure de la chaîne du polymère suivant laquelle les cristallites de téréphtalate de polyéthylène s'unissent aux chaînes flexibles de la partie amorphe, et forment une espèce de structure réticulaire semblable au pontage intermoléculaire.

# Zusammenfassung

Durch die Block-Polyadditionsreaktion des Diisocyanates mit linearen Polyestern, von denen einer Polyäthylen-

terephthalat war, wurden Polyester-Urethan-Blockcopolymere dargestellt. Die Schmelzpunkte der mehr als 30% Polyäthylenterephthalat enthaltenden Polyester-Urethan-Blockcopolymeren sind unabhängig vom zweiten Polyesterbestandteil, so dass die Kurve Schmelzpunkte gegen Bestandteile stufenartig ist. Andrerseits ist die Beziehung zwischen Einfriertemperatur und Bestandteilen des Blockcopolymeren, die gleiche wie für ein entsprechendes, statistisch aufgebautes Copolymers. Es wurde gefunden, dass einige Polyester-Urethan-Blockcopolymere, die 15-50% Polyäthylenterephthalat enthalten, elastische Eigenschaften haben; z.B. hat Polyäthylenterephthalat/Polyäthylenadipat (15:85)/Tetramethylendiisocyanat-Blockcopolymer eine Reissfestigkeit von 240 kg/cm<sup>2</sup> und eine Reissdehnung von 700%. Man kommt zu dem Schluss, dass diese elastischen Eigenschaften auf der Struktur de Polymerketten beruhen: die biegsamen Polymerketten in den amorphen Bereichen werden durch die Kristallite des Polyäthylenterephthalates zusammengehalten und so eine vernetzte Struktur aufgebaut.

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