

Extraction Fractionation of Segmented Polyurethanes According to Composition

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SYNOPSIS

Extraction of solid polyester-based segmented polyurethanes by chloroform and its mixtures with an increasing amount of *N,N*-dimethylformamide is described. Unlike the precipitation in a solvent–nonsolvent system, where fractionation according to the molecular weight dominates, the extraction can resolve the copolymer into fractions differing in the content of diisocyanate units. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Segmented polyurethanes (PUR) are multiblock copolymers of great practical importance which are prepared by the reaction of an oligomeric diol (e.g., dihydroxy-terminated polyether or polyester), a diisocyanate [e.g., 4,4'-methylene bis(phenyl isocyanate)] and a low-molecular-weight chain extender (e.g., butanediol). Oligomeric diols constitute "soft" segments whereas diisocyanate units form "hard" segments.¹ Polyurethanes behave as semicrystalline copolymers. Their soft segments are in a viscous or amorphous state whereas the hard segments usually form crystalline domains.

As most copolymers, polyurethanes are polydisperse in both molecular weight and composition. The polydispersity in molecular weight was studied by the precipitation fractionation^{2–5} or size exclusion chromatography.⁶ The compositional heterogeneity was the object mainly of theoretical studies^{7,8} and received little attention from experimentalists.⁶

A method which has been used with some success in many studies of the structural and compositional heterogeneity of semicrystalline homo- and copolymers is the successive extraction of the solid substance by solvents differing in the polymer–solvent interaction parameter.⁹ It is based on the theory of solubility of crystalline polymers.¹⁰ The solubility of

these substances is governed by the polymer melting temperature T_m^0 and the polymer–solvent interaction parameter χ , and except for short chains, it is almost independent of the chain length. The higher T_m^0 , the lower χ needed for dissolution at temperature T .

The melting temperatures of segmented polyurethanes are higher the higher the content of hard segments and, in general, are very high. Therefore, polyurethanes are soluble only in polar solvents such as *N,N*-dimethylformamide (DMF) and are merely swollen by less polar liquids (benzene, acetone, ethylacetate, chloroform) although the latter readily dissolve polyesters and polyethers constituting the soft segments.¹¹

In view of these facts we expected that polyurethane molecules, at least those containing a lower amount of hard segments, could be extracted by these solvents or their mixtures with DMF, which could be used for their fractionation according to composition. Experiments with polyester-based polyurethanes confirmed the expectation.

EXPERIMENTAL

Polymers

Polyurethane samples were laboratory products provided by Dr. R. Vondra (Svit Zlín, Czech Republic). They were prepared by the two-stage polymerization technique from an oligomeric dihy-

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droxy-terminated macrodiol (oligomers of ϵ -caprolactone, butylene adipate, or hexamethylene adipate), 4,4'-methylene bis(phenylisocyanate) (MDI), and butanediol in solutions in DMF. After diluting the final reaction mixture to 2% with DMF, the copolymers were isolated by precipitation into an excess of water and purified by reprecipitation from DMF into methanol. The precipitate was filtered off, washed three times with methanol, and dried to constant weight in vacuum at normal temperature. Most extraction experiments were made with sample PUR-1 prepared from 1 mol oligomeric ϵ -caprolactone ($\bar{M}_n \approx 2000$), 4 mol MDI, and 2.8 mol butanediol. The intrinsic viscosity in DMF at 25°C was $[\eta] = 0.74$ dL/g and the nitrogen content was 3.38%.

Extraction

A weighed amount of PUR was vigorously shaken at normal temperature with an excess of solvent (acetone, benzene, ethyl acetate, chloroform). At the end of the extraction the copolymer was filtered off and washed with the solvent. Then the procedure was repeated with four to six solvent-DMF mixtures containing subsequently 2 to 25% by vol DMF. The extracts were precipitated into an excess of methanol and the precipitates were treated as described above. Since the samples were swollen by the extracting liquid and the degree of swelling increased with an increase in the DMF content, filtration was slow and difficult. Squeezing the swollen sample was necessary to remove the remaining solution from the swollen gel.

Preliminary experiments were done with 0.5 g polymer and 10 mL solvent in each step. The time of extraction was 1 day per step. Large-scale Extractions I and II were carried out, respectively, with 2 and 20 g polymer and 50 and 500 mL solvent in each step (cf. Table I). The time of extraction was 1 day (Extraction I) and 1 week per step (Extraction II). The recovery was 83 (I) and 92% (II). With the other solvents and the other PUR samples, only preliminary (small-scale) experiments were made under similar conditions. Results of large-scale Extractions I and II of sample PUR-1 are summarized in Table I. Extraction by boiling solvents was made in a Soxhlet apparatus.

Refractionation of Primary Fractions

Fractions were dissolved in DMF and the solution (2% by wt) was heated to 80°C. Di-*n*-pentyl ether was slowly added under stirring until permanent

Table I Results of Extractions I and II of PUR-1

Extraction I				
Fraction	φ^a	p (%)	w^b	
I-1	0	2.62	0.02	
I-2	0.02	2.85	0.05	
I-3	0.04	3.01	0.07	
I-4	0.06	3.20	0.085	
I-5	0.10	3.25	0.20	
I-6	0.15	3.26	0.31	
I-7	0.20	3.33	0.21	
I-8 ^c		—	0.04	
Extraction II				
Fraction	φ^a	p (%)	w^b	$[\eta]^d$ (dL/g)
II-1	0.06	2.77	0.04	0.36
II-2	0.12	2.88	0.05	0.38
II-3	0.17	2.97	0.045	0.47
II-4	0.21	3.16	0.13	0.71
		(3.29)		(0.63)
II-5	0.25	3.32	0.61	0.74
		(3.36)		(0.69)
II-6 ^c		3.37	0.12	0.77
		(3.49)		(0.72)

^a Volume fraction of DMF in mixtures with chloroform.

^b Weight fraction of the extracted material.

^c Remainder.

^d Measured in DMF at 25°C.

Values of p and $[\eta]$ in parentheses were calculated from data for secondary fractions (cf. Table II).

cloudiness appeared. The cloudiness vanished by heating the solution to 85°C. The temperature was slowly (0.5°C/min) decreased under stirring to 65°C and the solution was left standing at this temperature. A viscous concentrated phase separated at the bottom and the upper (dilute) phase became limpid. After separating the concentrated phase, the dilute phase was cooled to successively lower temperatures. Concentrated phase in each step was dissolved in DMF and poured into an excess of methanol. The fractionation was finished at 22°C whereupon the solution was concentrated to one-tenth of its volume by evaporation in vacuum and precipitated by methanol.

Characterization of Fractions

The fractions were characterized by the intrinsic viscosity $[\eta]$ (in DMF at 25°C) and by elemental analysis [nitrogen content p (%)]. The latter was

Table II Results of Refractionation of Primary Fractions of PUR-1^a

(Extraction II)			
<i>t</i> (°C)	<i>w</i>	<i>p</i> (%)	[η] ^b (dL/g)
Combined Fractions II-1, 2, 3			
40	0.23	3.18	0.55
30	0.31	3.11	0.42
25	0.18	2.89	0.39
22	0.25	2.57	0.25
	0.02	—	—
Fraction II-4			
68	0.11	3.57	0.97
58	0.19	3.45	0.86
48	0.22	3.33	0.68
38	0.19	3.21	0.63
25	0.29	3.12	0.32
Fraction II-5			
68	0.25	3.56	0.95
58	0.19	3.48	0.73
48	0.17	3.41	0.69
38	0.17	3.30	0.62
25	0.22	3.03	0.42
Fraction II-6			
68	0.08	3.70	1.05
58	0.21	3.62	0.80
48	0.20	3.54	0.77
38	0.17	3.40	0.76
25	0.21	3.30	0.66
12	0.13	2.94	0.36

^a *t*, temperature of separation; *w*, weight fraction.

^b In DMF at 25°C.

converted into the weight fraction f_d of diisocyanate units by

$$f_d = p/p_d \quad (1)$$

where $p_d = 11.1\%$ is the nitrogen content in the MDI unit.

RESULTS AND DISCUSSION

Preliminary experiments were made with three PUR samples differing in the soft segment. The results were similar with all of them. Extraction with benzene, acetone, and ethylacetate was inefficient (yield less than 1%). With chloroform the yield was higher

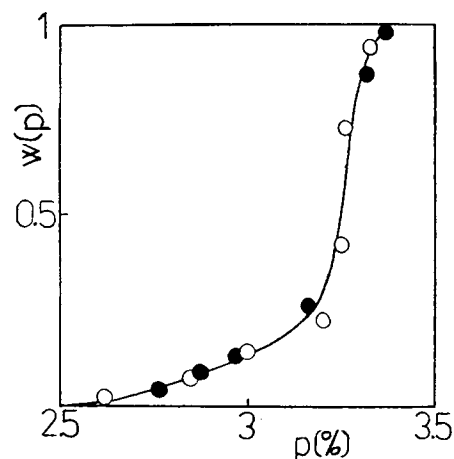


Figure 1 Cumulative distribution of composition (nitrogen content *p*) of PUR-1 Data points: Extraction I (○); Extraction II (●).

(2 to 6%). Extraction with boiling solvents was more successful, in particular with chloroform (10%). The nitrogen content of all of the obtained fractions was lower (2.5 to 3.1%) than in the sample before extraction. Preliminary experiments have also shown that mixtures of DMF with chloroform are more selective than those of DMF with benzene, acetone, or ethylacetate. For these reasons, large-scale experiments I and II (Tables I and II) were made with sample PUR-1 and mixtures of chloroform with DMF.

Table I shows that by successively extracting a solid PUR sample by chloroform and its mixtures with DMF, fractions with an increasing nitrogen content are obtained. Figure 1 presents cumulative compositional distribution curves based on primary fractions of Extractions I and II. The curves obtained by refractionating the primary fractions are presented in Figure 2. Those for fractions II-4, II-5, and II-6 almost overlap. The cumulative distribution curve of composition based on secondary fractions obtained by refractionation of primary ones is drawn in Figure 3.

The refractionation of primary fractions is based on the liquid-liquid phase equilibrium and, with respect to the results of previous studies,^{2,5} it was expected to proceed mainly according to the molecular weight. In fact, separations according to the molecular weight and composition (nitrogen content) superposed but the former prevailed. The intrinsic viscosities of secondary fractions amount to 50–130% of the [η] values of primary fractions, whereas the corresponding span of *p* values is only 90 to 110%.

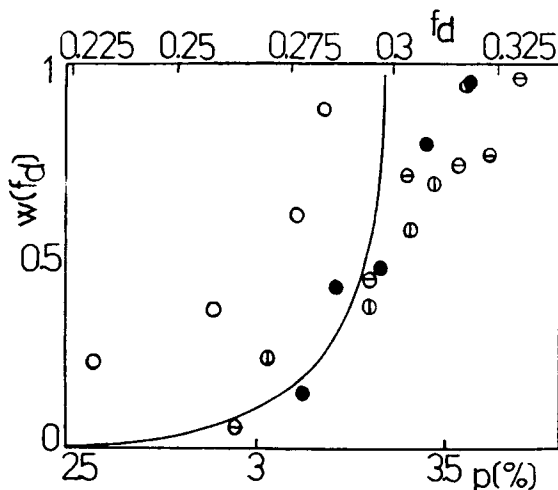


Figure 2 Cumulative distribution of composition of primary fractions obtained by refractionation. Data points for secondary fractions obtained from primary fractions (Extraction II): (○) combined II-1 to II-3; (●) II-4; (⊙) II-5; (⊕) II-6. Curve represents the cumulative distribution of PUR-1 (cf. Fig. 1). Composition is expressed in nitrogen content (p , %) or weight fraction f_d of diisocyanate units.

Figure 3 shows that the span of f_d values (0.225 to 0.33) is narrow. Lee et al.,⁶ who applied the size exclusion chromatography to a polyether-based polyurethane sample, obtained a similar result ($0.33 \leq f_d \leq 0.39$). Another interesting result (similar to the finding by Lee et al.⁶) follows from the plot of f_d vs $[\eta]$ (Fig. 4) for secondary fractions of Extraction II. It has an increasing trend and shows that the content of MDI units is lower in short chains.

The PUR sample was prepared by a two-stage process. In the first step (prepolymerization) the reaction took place between the polyol and MDI. The conditions were such that each molecule is terminated by an isocyanate unit at both ends. Thus, the mixture after the prepolymerization is supposed to contain unreacted MDI and prepolymer molecules DPD, DPDPD, DPDPDPD, etc., where P is polyol and D a diisocyanate unit (reacted by one or both isocyanate groups). In the second step of the synthesis (chain-extending reaction) the prepolymer components reacted with butanediol producing structures of the type



The weight fraction f_d of MDI units is

$$f_d = M_d n_d / (M_d n_d + M_p n_p + M_b n_b) \quad (2)$$

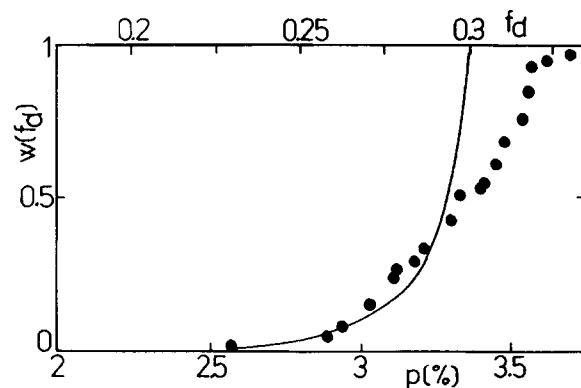


Figure 3 Cumulative distribution of composition of PUR-1. Data points (●) for secondary fractions (Extraction II). Curve represents the cumulative distribution constructed from the data for primary fractions (cf. Fig. 1). Notation of abscissa as in Figure 1.

where M_d and M_b are, respectively, the molecular weights of diisocyanate and chain extender groups, M_p is the (number average) molecular weight of polyol, and n_d , n_p , and n_b are the numbers of moles of MDI, polyol, and butanediol, respectively. By rearranging eq. (2) and substituting for $M_p = 2000$, $M_d = 252$, and $M_b = 88$, we obtain

$$f_d = [1 + 7.936(n_p/n_d) + 0.349(n_b/n_d)]^{-1} \quad (3)$$

Figure 5 shows that the effect on f_d of the term with n_b/n_d in eq. (3) is small in comparison with the effect of the first term. Variation in n_b/n_d between

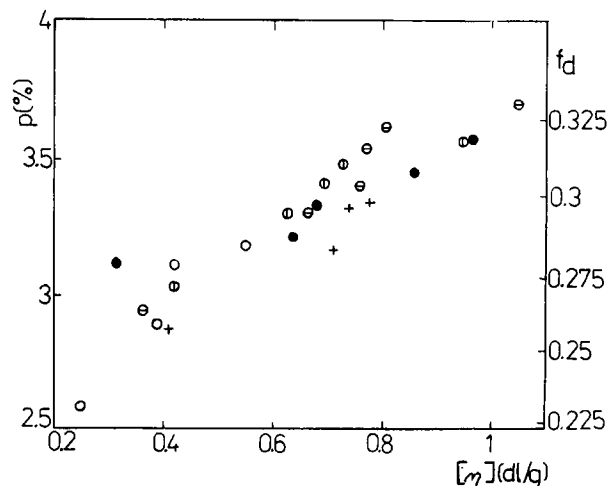


Figure 4 Correlation of composition of secondary fractions (Extraction II) with the intrinsic viscosity $[\eta]$ (DMF, 25°C). Notation of points as in Figure 2. Crosses (+) correspond to primary fractions. Composition in nitrogen content p or weight fraction of diisocyanate units f_d .

0.0 and 1 at a fixed value of n_p/n_d introduces a variation of less than 5% in f_d . So the ratio n_p/n_d can be estimated with fair accuracy from f_d . For the lowest and highest f_d values (0.22 and 0.33) we obtain $n_p/n_d \cong 0.4$ and 0.25, respectively.

An inspection of the formulas for the prepolymer molecules shows that the ratio n_p/n_d is zero for MDI and higher than $\frac{1}{2}$ for the other chains. The ratio n_p/n_d in the units DPDB, DPDPDB, DPDPDPDB, etc., formed during the chain extending reaction is that of the corresponding prepolymer chain (i.e., $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$, etc.) whereas it is zero for the DB units formed by the reaction of butanediol with MDI. Hence, incorporation of DB units lowers n_p/n_d below that for the corresponding prepolymer.

The numbers $n_{d,i}$ and $n_{p,i}$ in each molecule of the types described above are

$$n_{d,i} = a + 2b + 3c + 4d + \dots \quad (4)$$

$$n_{p,i} = b + 2c + 3d + \dots \quad (5)$$

If the MDI molecules were exhausted during the prepolymerization, so that no DB units could be produced during the second step, a would be zero. Hence

$$(n_{d,i})_{a=0} = 2b + 3c + 4d + \dots \quad (6)$$

Summing for all molecules leads to

$$n_p/n_d = \frac{1}{2} + (\frac{1}{2}C + D + \dots)/(2B + 3C + 4D + \dots) \quad (7)$$

where $B = \sum_i b_i$, $C = \sum_i c_i$, and $D = \sum_i d_i$, etc. Therefore, the ratio n_p/n_d would be higher than, or equal to, $\frac{1}{2}$.

However, experimental values of n_p/n_d are lower than $\frac{1}{2}$, indicating the presence of DB units produced by the reaction of MDI with butanediol in the chain extending step ($a > 0$). The higher n_p/n_d , the lower must be the content of these units. Therefore, as follows from Figure 4, the low-molecular-weight chains (low f_d and high n_p/n_d) were produced with a lower participation of the reaction of MDI with butanediol, i.e., with prevalence of the reaction of butanediol with DPD, DPDPD, etc.

CONCLUSIONS

The extraction of solid segmented polyurethanes by mixtures of chloroform with DMF resolves the sam-

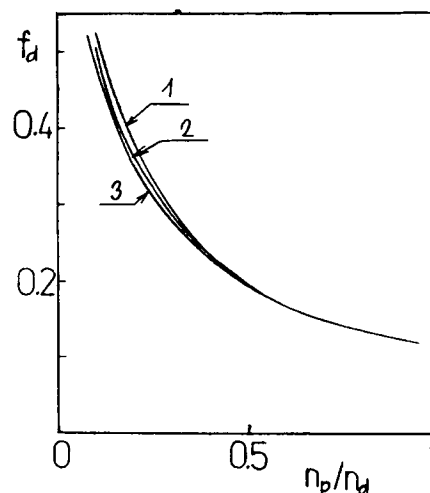


Figure 5 Dependence of the weight fraction f_d of MDI units on the ratio n_p/n_d . Curves 1 to 3 calculated with eq. (3) for $n_b/n_d = 0.1, 0.5,$ and 0.9 .

ples into fractions significantly differing in the content of diisocyanate units and can provide useful information on the compositional distribution of these copolymers.

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