

DETERMINATION OF COMPOSITION DISTRIBUTION OF SEGMENTED POLYURETHANES BY THIN LAYER CHROMATOGRAPHY

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ABSTRACT

The compositional heterogeneity has been studied for a series of PCL/MDI/BDO segmented polyurethanes. Their average hard segment content measured by NMR method was ranging from 17% to 42%. Macromolecules of segmented polyurethanes can be separated according to their composition by TLC technique with a mixed solvent of toluene/acetone/tetrahydrofuran as the developer. A dual wavelength TLC spectrodensitometer was used for quantitative analysis of TLC results, and method for data treatment is proposed to obtain the composition distribution with no need of any reference samples as TLC elution standards. The polyurethane samples are found to be heterogeneous in composition, having bimodal distribution curves.

INTRODUCTION

The macromolecules of segmented copolymers are usually considered to be statistically identical in chemical composition and average hard segment length. The microphase separation of hard and soft segments is used to explain the morphological features and properties of these copolymers. However, it has been found recently in the case of polyester/polyether^[1] and polyurethanes^[2] that because of the heterogeneity of the reaction system their molecules can be quite different in their chemical composition and hard segment length, and hence both microphase separation of segments and macrophase separation of molecules with different hard segment content should be considered. Since the heterogeneity, undoubtedly, will strongly affect the morphology and properties of these copolymers, it becomes necessary to have proper and convenient methods developed for its characterization. In a previous paper^[3] GPC technique with two detectors was used to characterize the compositional heterogeneity of a series of polyethylene terephthalate/polycaprolactone segmented copolymers. It is possible to get information about the composition distribution and average parameters characterizing the heterogeneity from the GPC data. However, the GPC technique is, in principle, of disad-

vantage to compositional characterization, because molecules are separated during GPC measurements according to the hydrodynamic volume of the molecular coils, which is dependent not only on the composition, but also on the molecular weight. It is yet impossible to separate the two factors, and the influence of molecular weight could not be neglected, so the composition distribution obtained from GPC measurements may be narrowed and the heterogeneity lowered.

Another effective technique for compositional analysis is thin layer chromatography (TLC). The composition distribution of some random copolymers and di- and tri-block copolymers, such as styrene/acrylonitrile, vinyl chloride/vinyl acetate and styrene/methyl methacrylate systems, has been studied by means of TLC technique^[4-7]. However no reports have been published describing the quantitative TLC studies of segmented copolymers. One of the main difficulties in dealing with segmented copolymers is the lack of proper standard samples. In this work the separation of polycaprolactone (PCL) based segmented polyurethanes by TLC according to their composition was studied, and the composition distribution of the polyurethane samples was obtained without any reference samples used as TLC elution standards.

EXPERIMENTAL

The synthesis of the segmented polyurethanes was carried out by a two-step method involving endcapping the hydroxy-terminated PCL ($M_n=1500$) with 4,4'-diphenylmethane diisocyanate (MDI) followed by reaction with the chain extender, 1,4-butanediol (BDO). Six samples were used, and their average composition are given in Table 1. The molar composition and the average hard segment content were determined from NMR data. The intrinsic viscosity was measured with solutions in dimethyl acetamide at 25°C.

Table 1 Polyurethane samples

Sample	Mole composition PCL/MDI/BDO	Aver. hard segment content (wt%)	Intrinsic viscosity (ml/g)
PU-1	1/1.18/0.18	17.2	107
PU-2	1/1.47/0.47	20.5	122
PU-3	1/1.84/0.84	25.3	107
PU-4	1/2.20/1.20	29.3	120
PU-5	1/2.60/1.60	33.4	125
PU-6	1/3.68/2.68	42.3	153

Commercial TLC plates, 20×20 cm, with silica gel were activated by heating at 110°C for 1 hr before use. Usually 20–40 μg polymer were deposited as spots by dropping 0.4% tetrahydrofuran solutions with a microsyringe along a line 2 cm above the bottom edge of the plate. The development was carried out at room temperature by ordinary method. When the solvent front advanced 10 cm away from the original spots, the development was stopped. The dried plate was then scanned in a Shimadzu dual-wavelength TLC scanning spectrodensi-

tometer model CS910. The wavelengths of the sample beams and the reference beams were $\lambda_s=250\text{nm}$ and $\lambda_r=350\text{nm}$ in the ultraviolet region and $\lambda_s=450\text{nm}$ and $\lambda_r=800\text{nm}$ for visible light respectively. The reflection absorption of the spots was detected by means of the double-beam and zigzag scanning techniques. Before scanning with visible light the plate was visualized by iod-treatment.

RESULTS AND DISCUSSION

From experiments with a variety of solvents of different solubility and polarity and their mixtures it was found that mixed solvent of toluene/acetone or toluene/acetone/tetrahydrofuran will give satisfactory separation of PCL/MDI/BDO segmented polyurethanes with average hard segment content ranging from 17% to 42%. In Table 2 are listed some of the experimental results obtained with ternary mixed solvents of toluene/acetone/tetrahydrofuran, while composition of 100/50/10 (volume ratio) was selected for use in this work for study of heterogeneity of the samples.

Table 2 R_f Values of samples from experiments with toluene/acetone/tetrahydrofuran mixtures as developers

Volume ratio	PCL	PU-1	PU-2	PU-3	PU-4	PU-5
100/40/10	1	0.50—0.65	0.45—0.55	0.38—0.50	—	0.30—0.42
100/50/5	1	0.60—0.75	0.60—0.68	0.50—0.60	0.45—0.55	0.35—0.50
100/50/10	1	0.70—0.80	0.65—0.73	0.50—0.68	0.45—0.60	0.45—0.58
100/60/10	1	0.75—0.90	0.70—0.83	0.60—0.77	0.60—0.70	0.50—0.65

The absorption data of a copolymer sample from the TLC scanning spectrodensitometer are the contribution of both components. Usually an additivity according to their content is supposed. For scanning with visible light ($\lambda_s=450\text{nm}$) the absorption

$$I(R_f) = k_h W(R_f) X(R_f) + k_s W(R_f) (1 - X(R_f)) \quad (1)$$

while in the case of scanning with radiation of wavelength $\lambda_s=250\text{nm}$

$$I'(R_f) = k'_h W(R_f) X(R_f) \quad (2)$$

as the soft segment is not sensitive to this wavelength. Proportional constants k_h , k'_h and k_s are the specific absorptions of hard and soft segments with respect to radiations of different wavelengths respectively. $W(R_f)$ is the amount of the copolymer at a given value of R_f , and $X(R_f)$ —the corresponding hard segment content of this copolymer fraction. The area under the absorption curve can be calculated as follows:

$$\begin{aligned} A &= \int I(R_f) dR_f = \int (k_h W(R_f) X(R_f) + k_s W(R_f) (1 - X(R_f))) dR_f \\ &= k_h W_0 \bar{X} + k_s (1 - \bar{X}) W_0 \end{aligned} \quad (3)$$

$$A' = \int I'(R_f) dR_f = \int k'_h W(R_f) X(R_f) dR_f = k'_h W_0 \bar{X} \quad (4)$$

W_0 is the amount of the sample deposited on the plate. $\bar{X}$ is the average hard segment content of the copolymer. The results of the polyurethane samples with different $\bar{X}$'s are shown in

Figs 1 and 2. The good linear dependence indicates the validity of equations (3) and (4), and parameters k_h , k'_h and k_s can be determined from these plots.

It may be supposed from the polarity of the soft and hard segments of the copolymer samples and the polarity of the mixture developer that in our TLC experiments the separation of copolymer molecules is controlled by the adsorption-desorption mechanism, i.e. according to the composition of the molecules. One of the methods that can be used to check the possible influence of other factors, such as molecular weight, is to compare the experimental data of function $X(R_f)$ for different samples. If the separation of the TLC experiment is only determined by the composition of the molecules, then the function $X(R_f)$ obtained for all of the samples in the same experiment should be identical. The function $X(R_f)$ can be obtained from experimental data $I(R_f)$ and $I'(R_f)$ according to equation (5), which is derived from equations (1) and (2) by eliminating $W(R_f)$ from them.

$$X(R_f) = k_s k'_h{}^{-1} (I(R_f)/I'(R_f) - (k_h - k_s)/k'_h)^{-1} \quad (5)$$

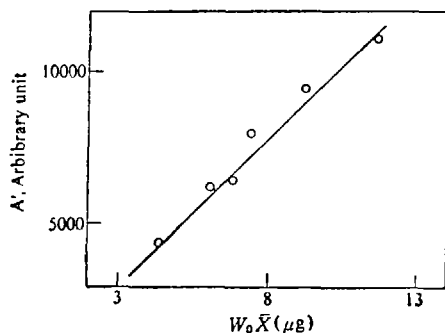


Fig. 1 $A'-W_0\bar{X}$ relationship

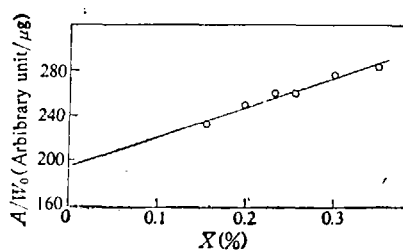


Fig. 2 $A/W_0-\bar{X}$ relationship

Results of all the six samples obtained in the same run are collected in Fig. 3. The R_f value increases monotonously with the increase in the soft segment content. No maximum or reverse phenomenon is found for the relationship between X and R_f . Besides, data of different samples grouped around a common curve with satisfactory coincidence. It could be concluded that in our TLC experiments the molecules of segmented polyurethanes are separated, at least, mainly according to their composition, and it is reasonable by means of the TLC method to get information about the real composition distribution of the segmented copolymers. It is clear from Fig. 3 that the used ternary mixed solvents are not effective in separating polyure-

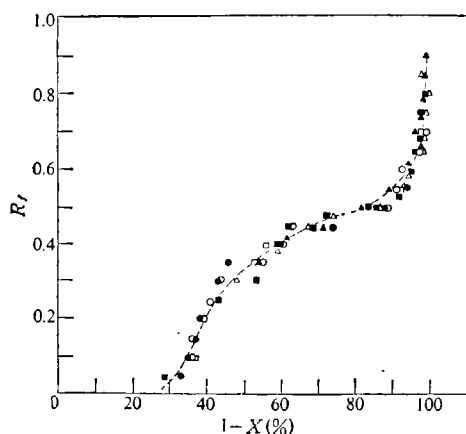


Fig. 3 Dependence of R_f on the composition of macromolecules

thane molecules with hard segment content higher than 70%. However it will not give serious influence on the results of composition distribution, as the hard segment contents of the samples are much lower than 70%.

Composition distribution of the samples may be obtained by combining functions $X(R_f)$ and $W(R_f)$, the letter can be determined from equation (2). Figs. 4 and 5 are the integral and differential weight distribution curves of the polyurethane samples PU-2 and PU-5 respectively. The distribution curves are more or less bimodal, having a small fraction of low hard segment content. For samples of higher hard segment content, like PU-4, PU-5 and PU-6, the hard segment content of this small fraction is around 10%. This implies that the actual synthesis process does not proceed ideally according to the hypothesis of uniform two-step

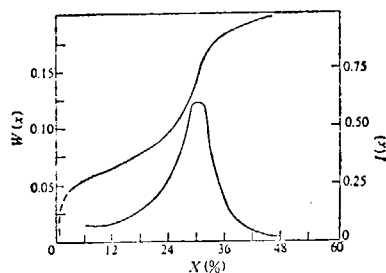


Fig. 4 Composition distribution curves of sample PU-2

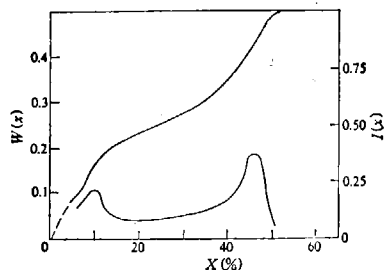


Fig. 5 Composition distribution curves of sample PU-5

method. The PCL soft segments of a small part of the copolymer molecules are mainly jointed with each other just by single MDI molecules. The distribution curves of samples PU-1, PU-2 and PU-3 indicate the existence of some unreacted pure PCL soft segments. These results are very similar to that of polybutadiene containing polyurethanes^[2] for which the existence of a low hard segment content fraction was evidenced by the appearance of two hard segment T_g 's and the results of extraction fractionation studies. Undoubtedly, the information from the composition analysis of segmented copolymers is valuable for its synthesis technology and for the control of the properties of its products.

The reproducibility of this technique has been checked, and satisfactory results have been observed. The relative difference between the values of parameters k'_h , k_h and k , determined from repeat measurements is usually less than 5%. A comparison of the distribution curves obtained by two measurements is given in Fig. 6.

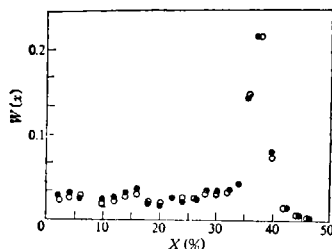


Fig. 6 Reproducibility test of the TLC measurements

CONCLUSIONS

1. Macromolecules of segmented polyurethanes PCL/MDI/BDO can be separated according to their hard segment content by TLC technique with toluene/acetone/tetrahydrofuran (100/50/10) mixture solvent as developer.

2. The composition distribution curve of segmented copolymers can be determined with satisfactory reproducibility from TLC data, if the average composition of these copolymers has been determined by other methods.

3. The PCL/MDI/BDO segmented polyurethanes are heterogeneous in composition, having bimodal distribution curves. The fraction of low hard segment content corresponds to molecules with their PCL soft segments connected mainly by single MDI molecules, or even unreacted PCL soft segments.

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