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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Relationship between Molecular Parameters of Linear Segmented Polyurethanes and Synthesis Conditions

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Abstract—A series of polyurethane samples were prepared, and the relationship between the molecular and rheological characteristics of the polymer, on the one hand, and the synthesis parameters, primarily the functional group ratio ([NCO]/[OH]), on the other hand, was examined.

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Syntheses of linear polyurethanes are complicated by the tendency of the principal monomer, diisocyanate, to undergo various side transformations along with the main reaction between isocyanate and hydroxy groups.

In this study we prepared a series of polyurethane samples from a polyester [poly(ethylene butylene adipate)] and toluene 2,4-diisocyanate (2,4-TDI) and examined how the molecular and rheological parameters of the product correlate with the synthesis conditions, primarily with the functional group ratio ([NCO]/[OH]).

EXPERIMENTAL

Samples of linear polyurethanes were prepared from the polyester (number-average molecular weight M_n = 2040), butenediol, and 2,4-TDI at various ratios of isocyanate and hydroxy groups, [NCO]/[OH] (0.5–0.99). The synthesis was performed in the bulk at 80–90°C using iron acetylacetonate as catalyst. The polyester : butenediol molar ratio was kept at 1.00 ± 0.01. The samples obtained were examined by gel chromatography (Waters two-detector unit). We also determined the intrinsic viscosity of the samples (solvent methyl ethyl ketone, 25°C) and dynamic viscosity of 20% solutions in ethyl acetate (Hoeppler rheoviscometer, 25°C).

Figure 1 shows the theoretical dependences of the number-average (calculated from the ratio of isocyanate and hydroxy groups) and weight-average molecular weights on the [NCO]/[OH] ratio. Analysis of the real samples showed that their average molecular weights at [NCO]/[OH] > 0.8 were somewhat lower than those calculated theoretically assuming that the urethane formation reaction was complete (Fig. 1). The differences between the calculated and experimental weight-average molecular weights reach 10–15 rel. %. A similar pattern is observed with the number-average molecular weight.

The difference between the calculated and experimental molecular weights increases with an increase in the [NCO]/[OH] ratio in the range 0.95–0.99 (from the technical viewpoint, the most

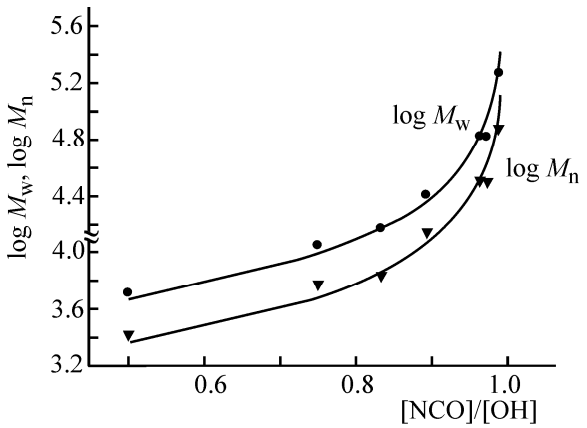

Fig. 1. Calculated (curves) and experimental (points) number-average and weight-average molecular weights as functions of the [NCO]/[OH] ratio.

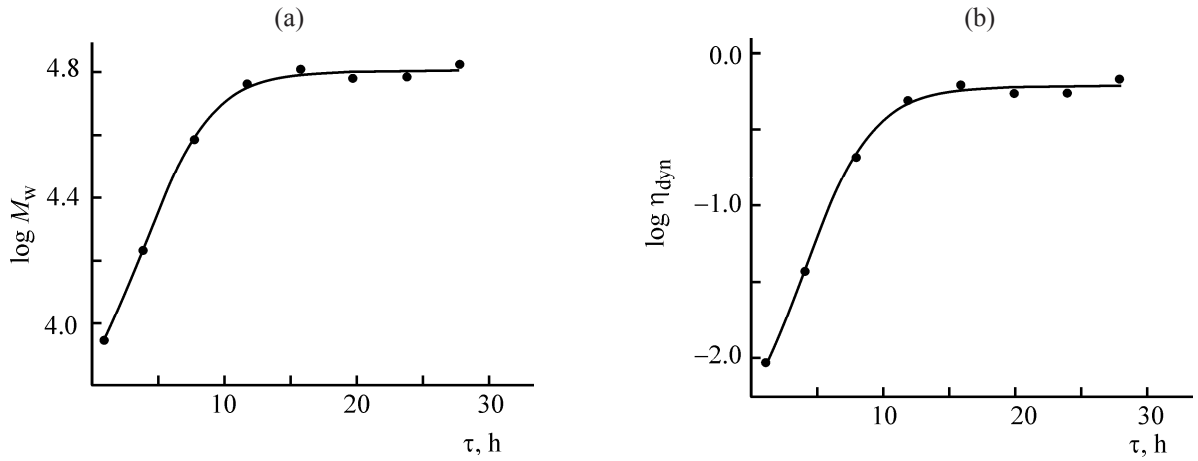

Fig. 2. (a) Molecular-weight and (b) rheological parameters of rubber as functions of thermostating time τ. (M_w) Weight-average molecular weight and (η_{dyn}, Pa s) dynamic viscosity.

appropriate are the ratios [NCO]/[OH] = 0.94–0.97). Four major groups of factors affecting M_w and M_n of polyurethane can be distinguished: (1) accuracy of determining the content of NCO and OH groups in the starting substances and hence the accuracy of the calculated [NCO]/[OH] ratio; (2) degree of reaction completion with respect to isocyanate groups; (3) possible occurrence of side reactions involving highly reactive isocyanate groups; and (4) presence of cyclic compounds in the polyester.

As for the first factor, it is known that the accuracy of determining the content of hydroxy groups in the polyester and of NCO groups in the diisocyanate is about 2 and 1 rel. %, respectively. The main substance content in the technical-grade 2,4-TDI may vary within 98–99.5%. Apparently, the above errors in determination of the functional group content in the polyester and 2,4-TDI considerably decrease the reliability of the [NCO]/[OH] ratio set in the course of the synthesis. Comparison of the calculated and experimentally determined molecular weights of the polyurethanes obtained shows that satisfactory results can be obtained only when the error in determining the [NCO]/[OH] ratio does not exceed 0.4 rel. %.

As the hydroxyl-containing components are in excess, the conversion of NCO groups is about 100%. This conversion is attained by heating the polyurethane at ~80–90°C for 1 day. Attainment of constant characteristics of the product is confirmed by determination of the molecular and rheological parameters (Fig. 2). It should be noted that longer thermostating leads to a certain decrease in the viscosity. This trend is due to competition of the polymer degradation across ester bonds, involving atmospheric moisture, with the main reaction NCO–OH. High viscosity of the polyurethane bulk may make 100% completion of the main reaction impossible because of steric hindrance. The product characteristics were stable in storage [1]. We were able to reproducibly prepare the product with M_w of up to ~80000–100000 and M_n of ~40000–50000 (i.e., with the degree of polycondensation of ~40–50).

In the course of the synthesis, certain side reactions involving isocyanate groups [2] are inevitable: loss of isocyanate groups due to reaction with traces of moisture (drying of the polyester–glycol mixture allows the water concentration to be decreased to 0.02%); trimerization via isocyanate groups, giving rise to branched structures (model experiments showed that the contribution of the trimerization is insignificant when OH groups are in excess); allophanate formation and other processes typically occurring in synthesis of polyurethanes.

All the above reactions lead to a certain decrease in the effective NCO/OH ratio, causing formation of a product with a somewhat lower molecular weight, compared to the calculated value [3].

It should be emphasized that it is extremely difficult to describe quantitatively fluctuations of the main factors of the synthesis (accuracy of the [NCO]/[OH] ratio, degree of reaction completion, side reactions) and to evaluate the contribution of each factor to characteristics of the finished product. Therefore, the best way to prepare relatively high-molecular-weight

Molecular-weight parameters of poly(ester urethanes), according to the data of two-detector gel permeation chromatography

Run. no.	Refractometer				Photometer			
	M_w	M_n	M_w/M_n	LMWF content, %	M_w	M_n	M_w/M_n	LMWF content, %
1	15418	8281	1.87	5.0	15588	7104	2.05	2.6
2	25560	14470	1.77	4.0	5080	14050	1.79	2.6
3	47000	24480	1.92	5.0	46510	25010	1.86	1.8
4	52260	29190	1.79	3.5	51210	28270	1.88	2.1
5	56940	31780	1.85	2.8	55880	29340	1.90	2.1
6	72930	38300	1.90	4.6	71500	36660	1.95	2.5
7	95660	40020	2.39	2.4	94870	38400	2.47	1.8
8	188170	75980	2.48	5.6	184580	71580	2.58	2.8

polyurethanes is correction of the [NCO]/[OH] ratio (as a rule, toward higher values), based on the results of a preliminary experiment. This procedure allows fairly quick determination of the [NCO]/[OH] ratio ensuring formation of a product with the preset molecular weight and dynamic viscosity, without considering particular factors that complicate calculation of the required [NCO]/[OH] ratio.

It is known that synthesis of polyesters is accompanied by formation of cyclic compounds of adipic acid with glycols. Naturally, in the course of polycondensation, rings are preserved, and new cyclic structures can also be formed from the diisocyanate and glycols (and also of low-molecular-weight polyester fragments). The gel chromatograms of the polyurethanes contain an extended low-molecular-weight "tail" corresponding to cyclic and low-molecular-weight fragments of the polyester and polyurethane (see table). The fraction of these fragments varies within 4–6 (with refractometric detector) or 2–3 wt % (with photometric detector). The difference in the content of the low-molecular-weight fraction according to the data of two detectors is due to the fact that the photometer detects fragments containing an isocyanate moiety, and the refracttometer, all the components of the low-molecular-weight fraction (LMWF). It should be emphasized that inclusion of low-molecular-weight fragments in calculation of MWD parameters results in a sharp increase in the polydispersity coefficient of the polyurethane (to 3.5–4.5). The main module of the distribution (without taking into account LMWF), corresponding to M_w/M_n = 1.8–2.1, is well consistent with the theoretical value of ~2.0. Thus, to characterize linear polyurethanes more comprehensively, it is appropriate to calculate both MWD of the major component and the total distribution spectrum [4].

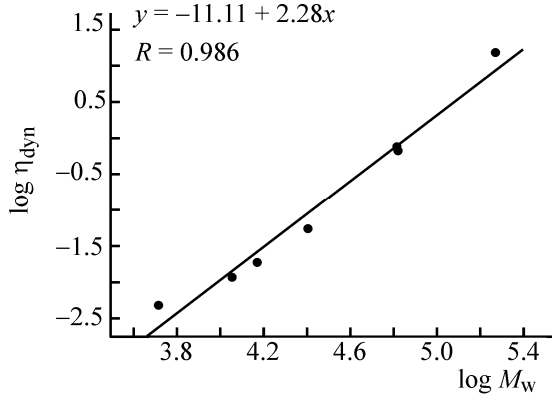

Fig. 3. Dynamic viscosity η_{dyn} (Pa s) as a function of weight-average molecular weight M_w (log–log plot).

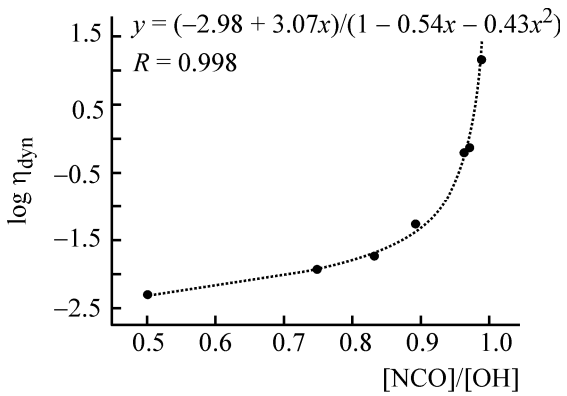

Fig. 4. Dynamic viscosity η_{dyn} (Pa s) as a function of the functional group ratio [NCO]/[ROH] (semilog plot).

Essentially similar values of the molecular weights determined using the two detectors (see table) suggest that the distribution of isocyanate units in the polymer chain is uniform, i.e., the polymer chain has a segmented structure.

An important technical characteristic of segmented polyurethanes is the dynamic viscosity of polymer solutions, which quite satisfactorily correlates with the weight-average molecular weight of polyurethanes (Fig. 3). The linearity of this logarithmic dependence indirectly suggests the lack of significant branching that could be caused by possible reactions involving NCO groups. Certain deviation of this dependence from linearity in the low-molecular-weight region may be due to a change in the structure of the polyurethane in going from the lowest-molecular-weight product ([NCO]/[OH] = 0.5) to polymers of virtually the same composition, according to the scheme polyester–TDI–BD → (polyester–TDI–BD–TDI)$_n$(BD or polyester).

In this case, the content of urethane groups in the polyurethane increases from 5 to 9 wt %. The dynamic viscosity η_{dyn} of concentrated polyurethane solutions sharply increases with an increase in the main synthesis parameter, [NCO]/[OH] (Fig. 4). The equations correlating the main parameters of the system ([NCO]/[OH], M_w, η_{dyn}) show that the dynamic viscosity of the solution depends on the [NCO]/[OH] ratio raised to a fairly high power, which is a consequence of steeply ascending dependences of M_w on [NCO]/[OH] and then, of η_{dyn} on M_w.

CONCLUSIONS

(1) The dependence of the molecular-weight characteristics of the polymer on the ratio of the reactive functional groups [NCO]/[OH] and the major factors negatively affecting the effective [NCO]/[OH] ratio were determined.

(2) The possibility of optimizing the polyurethane synthesis and preparing polymers with preset molecular-weight and rheological characteristics was demonstrated.

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