Properties of Cast Urethane Elastomers Prepared from Poly(ε-caprolactone)s

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Synopsis

General information on the methods of lactone polymerization has been given. The method applied in this study for obtaining poly(ε-caprolactone) with the use of sodium derivatives of ethanediol, diethylene glycol, 1,5-pentanediol, and 1,10-decanediol has been discussed, and the results of the experiments have been given. The properties of cast urethane elastomers prepared from the obtained poly(ε-caprolactone) have also been presented.

INTRODUCTION

Among polyesters used for preparing urethane elastomers worthy of mention is a group of intermediate products obtained from lactones. The reasons for drawing attention to that group of intermediate products are their characteristic chemical structure and the methods of obtaining them. Further, this group distinguishes itself by the properties of urethane elastomers obtained from it. In comparison with their analogues obtained from polyesters prepared by polycondensation of dicarboxylic acids with glycols, the urethane elastomers synthesized from polycaprolactones have a higher hydrolytic resistance and better properties at low temperatures.[1] Polyesters prepared from lactones have a slightly different chemical structure than their analogues synthesized by polycondensation of dicarboxylic acids with glycols. The differences consist of the facts that in the case of polycaprolactone the methyl groups are always between the oxygen atoms and the carboxylic groups and that in the polyesters prepared from carboxylic acids and glycols the methyl groups are placed between the oxygen atoms (glycol part) and the carboxylic groups (acid part). Thus, a more regular structure appears in polyesters prepared from lactones, which undoubtedly has an influence on the properties of the urethane elastomers.[2] Brode and Koleske[3] have proposed the following division of the systems used for polymerization of lactones: active hydrogen initiator, no catalyst, e.g., ROH, RNH_2, etc.; nonactive hydrogen initiator, or catalyst only, e.g., R_2Zn, $Sn(OR)_2$ or $Sn(OR)_4$, etc.; active hydrogen initiator plus catalyst of, e.g., ROH + $Ti(OR)_4$, etc.

The basic method of polylactone synthesis as applied at the Union Carbide Co.,[4] the well-known producer of intermediate products of this type, is based on the use of initiators with active hydrogen atoms, e.g., glycols, diamines, hydrozine, semicarbazones, and oximes. It is recommended to carry out polymerization of lactones at a temperature of 120–200°C, the process being of various

durations (up to 7 days) and dependent on the kind of lactone and initiator applied.

Ethanoloamine may also be used for initiating the polymerization of δ-valeroactone.[3] Estrina and co-workers[5] have shown that polymerization of ϵ-caprolactone in the presence of aniline and m-phenylenediamine carried out at raised temperature, after opening of the lactone ring, due to expansion of the alkyl–oxygen bond, proceeds according to the anion mechanism with ammonocarboxylic ionic centers.

Shiota and co-workers[6] used sodium acetate and toluenesulphonic acid as well as their soda derivatives for polymerization of β-propiolactone. Proton acids[2] and Lewis acids, e.g., $AlCl_3$ as well as trifluoroacetic anhydride aluminum trichloride (1:2) and boron compounds, e.g., acyl fluoroborates as well as complex of boron trifluoride etherate[7] find application in cationic polymerization. In anionic polymerization of lactones such catalysts as alkali metals, naphthalene sodium, organometallic compounds, tertiary amines, alkali metal halides, carboxylic acid salts with alkali metals cations, and alcoholates are used.[8-13] Słamkowski and Penczek[14] as well as Deffieux and Boileau[15] have found that an addition of dibenzo-18-crown-6-ether and dicyclohexyl-18-crown-6-ethers accelerates polymerization of lactones carried out in the presence of KOH, KCl, NaCl, KcNs, CH_3COONa, and potassium $tert$-butoxide. Polymerization of lactones carried out with the use of methanol or ethanol with an addition of sodium naphthalene is an example of the process realized with a system of initiators containing active hydrogen and catalyst atoms. An interesting example of lactone polymerization has been described by Perret and Skoulios.[16] They subjected poly(oxyethylene glycol) to the action of naphthalene sodium and applied the obtained sodium derivative as an inhibitor at the polymerization of ϵ-caprolactone. In the results block copolymer of the following type was obtained:

$$\text{-------PCL---POE---PCL-------}$$

where PCL = poly(ϵ-caprolactone) and POE = polyoxyethylene. Triblock copolymers were also obtained by Nobutoki and Sumitomo[17] with the use of a living polysterene as an initiator for polymerization of ϵ-caprolactone. Taking advantage of the method proposed by Perret and Skoulios,[16] sodium derivatives of ethanediol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, and 1,10-decanediol have been obtained in this study. Further, they were used as initiators for the polymerization of ϵ-caprolactone. Finally, five various oligomers were obtained and then used for the synthesis of cast urethane elastomers. Properties of the cast urethane elastomers obtained have been given in this study.

EXPERIMENTAL

Materials. Before being used for polymerization (dehydrated and oxygenfree) ϵ-caprolactone of Merck production was distilled under argon with 1% of 4,4'-diphenylomethane diisocyanate added. At reduced pressure of ca. 150 Pa the boiling fracture was collected at a temperature of 70–71°C. Ethanediol diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,10-decanediol (Polskie Odczynniki Chemiczne, Fluka, Merck) were distilled before use under reduced pressure and under oxygen- and humidity-free argon. Sodium naphthalene was

obtained according to the prescription given by Scott and Walker[18] with tetra-hydrofuran applied as solvent. Tetrahydrofuran (Polskie Odczynniki Chemiczne) was heated at boiling temperature under a reflux condenser with 1% of 4,4'-diphenylmethane diisocyanate added during 1 h. Then, it was distilled under oxygen- and humidity-free argon and the boiling fraction collected at 63–67°C. The 4,4'-diphenylmethane diisocyanate (Desmodur 44MS) of Bayer production had a concentration of 99.6% as determined by the amine equivalent method.[19]

Measurements. The mean molar weight number of the obtained poly(ϵ-caprolactone) was determined by osmometry by means of a Knauer apparatus using THF as solvent. For the sake of comparison, mean molar weights were also determined of the obtained polymers by determining hydroxyl groups by Warley's method.[19] The transformation degree in the poly(ϵ-caprolactone)s synthesis was determined as follows. Samples of the reaction mixture (ca. 4.5 g) were taken from the reactor, dissolved in 10 cm^3 THF and precipitated with n-hexane (ca. 50 cm^3). Rests of the solvents were removed from the isolated oligomer (decantation of filtration) and weighed. Further, the degree of transformation was calculated. The macroscopic properties of the obtained cast urethane elastomers were determined in compliance with the Polish Standard Specifications involved. Measurements of thermomechanical properties of the urethane elastomers were taken by means of an apparatus which had been constructed at the Polymer Institute of the Łódź Technical University. Samples in the form of 50 × 10 × 1 mm strips were used for the measurements.

Electron-microscopic tests of the obtained elastomers were carried out as described below. A polymer sample was cooled in liquid nitrogen and a fracture made. A film of poly(vinyl alcohol), using a 5% solution of it in water, was applied on the surface of the fracture. The obtained matrix with fixed relief at the surface of the fracture was shaded at an acute angle with platinum, and then influxed with coal. After dissolving in water the matrix, poly(vinyl alcohol), the obtained platinum–carbon replica of the surface of the elastomer fraction was observed directly in an electron microscope (Tesla, Type BS-613) at a voltage of 80 kV. Electron-microscopic graphs of the tested elastomers are given in Figures 1–5.

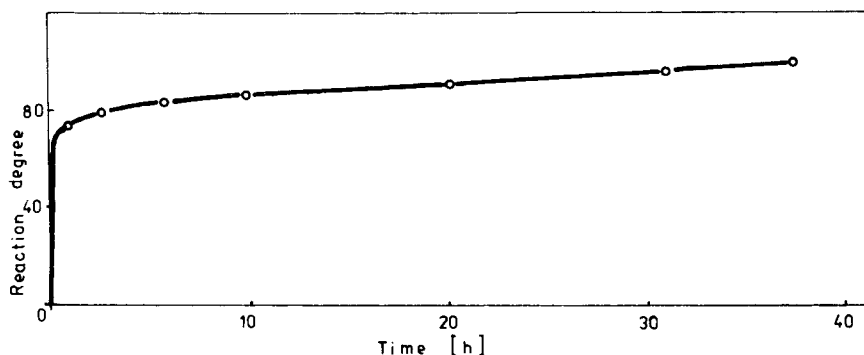**Synthesis of Poly(ϵ-caprolactone)s.** 0.08 mol of the relevant glycol was

Fig. 1. Change of the transfer degree in the function of time for the synthesis of poly(ϵ-caprolactone) carried out with the use of sodium derivative of 1,4-butanediol.
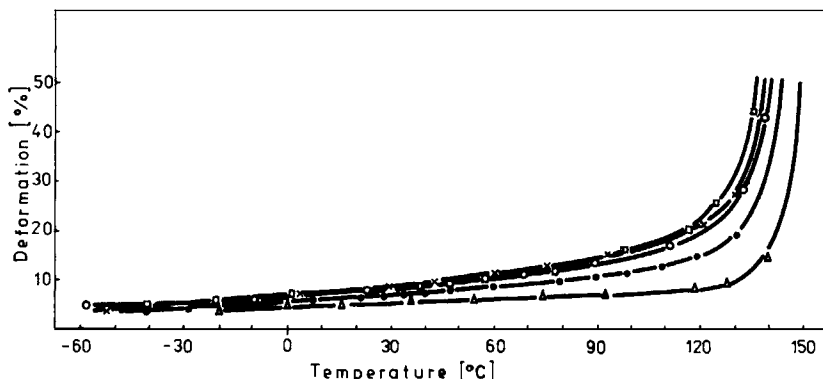
Fig. 2. Thermomechanical of urethane elastomers obtained in subsequent tests: (×) R-28; (●) R-23; (O) R-29; (□) R-24; (△) R-25.

placed in a typical glass reactor of 500 cc which was provided with a stirrer, a thermometer, and a reflux condenser under argon. While keeping up the atmosphere of inert gas and intensive stirring, stoichiometric quantities of sodium naphthalene in the form of solved THF were added from a special burette. The end of adding sodium naphthalene was determined by the appearance of a greenish color of the contents in the reactor. Then, a determined amount of ε-caprolactone, following from a predetermined molar ratio of the initiator to the monomer as given in Table I, was added to the newly prepared sodium derivative of the appropriate glycol. At continuous changing of heating, the polymerization was carried out under argon during a previously determined time, as given in Table I, so as to ensure a maximum capacity of the process. On completion of the synthesis, the obtained solid product was dissolved at room temperature in THF and then neutralized by means of saturated solution of HCl in THF. The solutions of the obtained oligomers were subjected to rotational evaporation, and the solvents were removed under vacuum. The obtained samples of poly(ε-caprolactone), after determination of their mean molar weights, were used for the synthesis of cast urethane elastomers.

Synthesis of Cast Urethane Elastomers. The synthesis of urethane elastomers was carried out in a two-stage method as described below. A typical glass reactor of 500 cc provided with a stirrer, a thermometer, and a glass adapter was filled with anhydrous $CaCl_2$ and 0.04 mol of an appropriate poly(ε-caprolactone) added. The content was heated at a temperature of 120°C under vacuum of ca.

TABLE I
Conditions at Synthesis of Poly(ε-caprolactone)

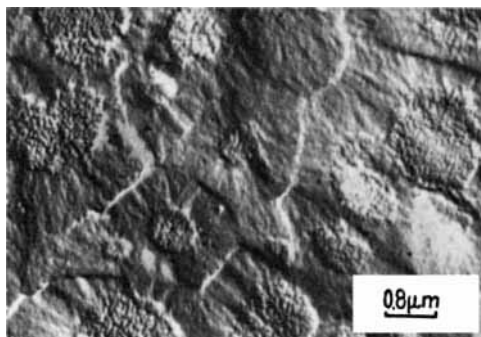| Item no.	Synthesis symbol	Initiator: sodium derivative	Duration of polymerization at 120°C (h)	Transverse degree (%)
1	R-28	Diethylene glycol	17	95
2	R-23	Ethanediol	25	95
3	R-29	1,4-Butanediol	38	100
4	R-24	1,5-Pentanediol	50	100
5	R-25	1,10-Decanediol	40	74.5

Fig. 3. Electromicroscopic photo of brittle fracture of urethane elastomer obtained in test R-25 (sodium derivative of 1,10-decanediol).

150 Pa during 1 h. Then, at intensive stirring, 0.16 mol of 4,4'-diphenylomethane diisocyanate heated up to a temperature of ca. 60°C was added. The synthesis of urethane elastomer was carried out at 120°C up to 20 min. While continuing to heat and stir during the next 10 min, the synthesis was carried out under vacuum of 150 Pa. Concentration of free isocyanate groups in the obtained prepolymer was determined by the amine equivalent method.[19]

In the second stage precisely dehydrated 1,4-butanediol was added to the obtained prepolymer at 100°C in the quantity which followed from the assumed molar ratio free NCO/glycol OH = 1.07. After 1 min of stirring, the mixture was poured into a centrifuge basket heated up to 110°C (ca. 2000 rpm). After 20 min the initially formed foil of cast urethane elastomer, ca. 2 mm thick, was placed in a drier and heated at 120°C during 24 h. The obtained elastomer samples were subjected to the foreseen tests.

RESULTS AND DISCUSSION

The results of investigation as represented in Figure 1 and Table I show that polymerization of ε-caprolactone carried out with the use of sodium derivatives of various glycols takes place at quite a considerable velocity. Butanediol-sodium-derivative-initiated polymerization of ε-caprolactone attains a trans-
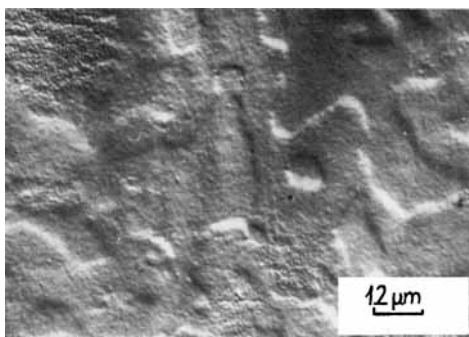

Fig. 4. Electromicroscopic photo of brittle fracture of urethane elastomer obtained in test R-29 (sodium derivative of 1,4-butanediol).
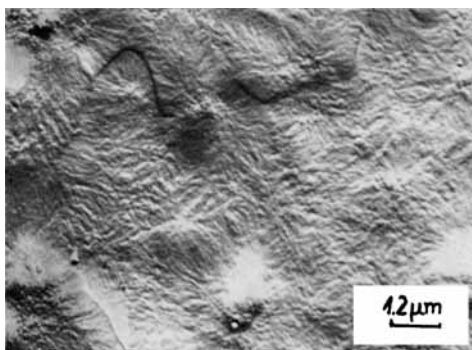
Fig. 5. Electromicroscopic photo of brittle fracture of urethane elastomer obtained in test R-28 (sodium derivative of diethylene glycol).

formation degree of 0.78 as soon as after 1 h, and the complete process is finished after 38 h. The data given in Table II indicate additionally that the kind of glycol used in the form of sodium derivative has an effect on the course of ϵ-caprolactone polymerization. When sodium derivative of diethylene glycol was applied, the polymerization was completed as early as after 17 h. In the case of several glycols from ethanediol to decanediol the time necessary for the completion of ϵ-caprolactone polymerization increases with the increasing number of carbons in the hydrocarbon chain. This seems to suggest that, as the glycol hydrocarbon chain extends, the catalytic activity of the initiators applied decreases. That is why when decanediol sodium derivative was applied during a comparable time of 50 h, a lower degree of transformation was obtained than in a similar synthesis carried out with the use of pentanediol sodium derivative. The results of measurements, compiled in Table II, indicate that the molecular masses of the obtained polymers, determined by osmometry and chemically, are quite close to the results expected on the basis of the magnitude of the molar ratio of the initiator to the monomer applied in carried-out syntheses. The appearing differences between M_{calcd} and M_{os} as well as of M_{OH} in the polymers obtained with the use of decanediol sodium derivative most probably follow from the distinctly

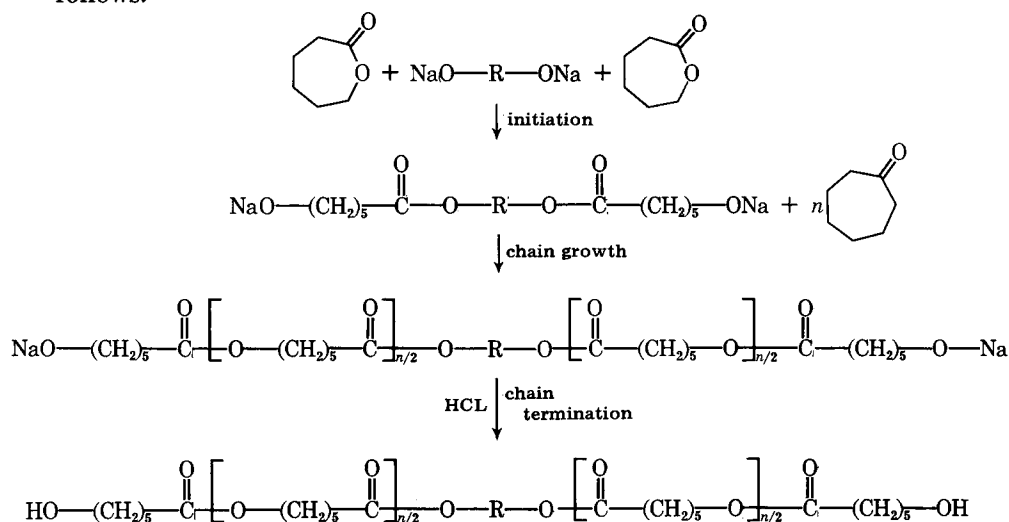TABLE II
Measurement Results of Mean Molar Weights of Poly(ϵ-caprolactone)

Item no.	Synthesis symbol	Molar ratio initiator/monomer			M_{calcd}[a]	M_{os}[b]	M_{OH}[c]
		Initial in synthesis	Calc on basis of				
			M_{os}[b]	M_{OH}[c]			
1	R-28	1/15.8	1/19.6	1/16.7	2000	1815	2020
2	R-23	1/17	1/15	1/14.2	1910	1742	1682
3	R-29	1/17	1/16.8	1/17.8	2030	2000	2115
4	R-24	1/17	1/13.3	1/16.5	2040	1625	1910
5	R-25	1/17	1/8.7	1/8.3	2110	1165	1120

[a] M_{calcd} = mean molecular weight calculated on the basis of the initial molar relation initiator–monomer applied in the synthesis.

[b] M_{os} = mean molecular weight as determined by means of Knauer's apparatus.

[c] M_{OH} = mean molecular weight as established on the basis of determinations of the content of hydroxyl groups by Vorleay's method.[19]

lower degree of transformation in comparison with that in the other syntheses. The obtained values of mean molar weights M_{os} and M_{OH} as well as the close values of the calculated molar ratios of the initiator to the monomer in relation to those assumed in the synthesis, with the justified exception for the decanediol sodium derivative, suggest that ϵ-caprolactone polymerization carried out with the use of sodium derivative of the tested glycols takes place according to similar mechanisms as given by Yamashito and co-workers[11] for alcoholate initiators. The polymerization course ϵ-caprolactone may be presented schematically as follows:

Further, the data given in Table II suggest that in general a high conformability of the results of M_{os} and M_{OH} determinations was obtained.

Properties of Cast Urethane Elastomers

Properties of the cast urethane elastomers prepared from the poly(ϵ-caprolactone)s obtained are compiled in Table III. The urethane elastomers obtained from those poly(ϵ-caprolactone)s have a quite favorable set of macroscopic properties. The effect may also be seen of the glycol sodium derivative on the properties of the obtained polymers. The urethane elastomer obtained from the poly(ϵ-caprolactone) prepared with the use of ethanediol sodium derivative has the highest tensile strength and rigidity expressed as the stress at 300% elongation. This polymer, besides the urethane elastomer obtained from poly(ϵ-caprolactone) prepared in the presence of decanediol sodium derivative, is also characterized by the lowest relative at break. The latter polymer as well as that obtained from poly(ϵ-caprolactone) prepared with the use of pentanediol sodium derivative have the highest tearing strength. Urethane elastomers which have rests of pentanediol and butanediol in their structure are characterized in turn by the highest elasticity. The urethane elastomers obtained also have various hardness values. The urethane elastomer containing the rests of the ethylene glycol in its structure has the lowest hardness. A comparison of the macroscopic properties of the obtained urethane elastomers with those of similar products described in literature[20,21] indicate that the poly(ϵ-caprolactone)s

TABLE III
Properties of Cast Urethane Elastomers

Properties	Type of Poly(ϵ-caprolactone)				
	R-28, diethylene glycol	R-23, ethane-diol	R-29, 1,4-butane-diol	R-24, 1,5-pentane-diol	R-25, 1,10-decane-diol
Concentration of free NCO groups in polymer	6.3	8.9	7.0	9.1	11.4
Molar ratio NCO to OH in synthesis of cast urethane elastomers	1.07	1.07	1.07	1.07	1.07
Shore hardness	72	89	76	90	96
Stress at (% elongation in MPa)					
50	2.1	5.9	2.4	—	13.2
100	3.3	7.7	3.3	—	14.8
200	—	11.3	4.7	—	—
300	7.8	17.3	6.6	13.3	—
Tensile strength at break (MPa)	27.4	31.4	22.5	22.5	26.5
Elongation (%)	500	440	580	580	440
Tearing strength (kN/m)	68.6	53.3	52.5	85.2	142.2
Elasticity (%)	24	23	29	32	22

obtained by us give the possibility of preparing elastomer materials with similar features. The results of the measurements of thermomechanical properties as compiled in Figure 2 indicate that a rest of hydrocarbon from the initiator also has an effect on the thermal resistance of the elastomers obtained. The examined elastomers keep up their properties at raised temperatures relatively well. This may be especially seen when the rest of the decanediol appears in the elastomer chains, in which case changes of elongation of the sample under load are negligible even at the temperature range up to 140°C. This urethane elastomer is also characterized by higher flow temperature in comparison with that of the remaining elastomers.

Electron-Microscopic Tests

An analysis of the electron-microscopic data given in Figures 3–7 shows that the urethane elastomers obtained have a quite diversified morphology of the

Fig. 6. Electromicroscopic photo of brittle fracture of urethane elastomer obtained in test R-23 (sodium derivative of ethanediol).
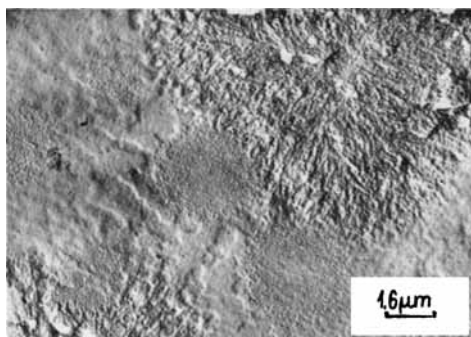
Fig. 7. Electromicroscopic photo of brittle fracture of urethane elastomer obtained in test R-24 (sodium derivative of 1,5-pentanediol).

surface of the brittle fracture. The electron-microscopic graphs show that the polymers obtained have continuous and dispersed phases. Furthermore, the continuous phase as well as the dispersed one have a diversified structure. In the continuous phase it is possible to distinguish spherulite structures of various dimensions and a structure of interpenetrating phases. The above-mentioned morphological phase is distinctly found, especially in those urethane elastomers that contain in their structure the rest of the decanediol (sample R-25, Fig. 3), spherulitelike phase, and butanediol (sample R-29, Fig. 4), interpenetrating phases. Some of the polymers do not have such a distinctly marked structure of the continuous phase (sample R-28, Fig. 5, and sample R-23, Fig. 6). Morphological diversification of the dispersed phase resolves itself to the appearance of two types of granular aggregates. Those aggregates have a distinct shape in the urethane elastomer which contains rests of pentanediol (Fig. 7) in its structure. One type of the dispersed phases (I) is composed of fine grains located on the flat surface of the fracture, and the other type (II), which is in most cases bigger, is composed of grains located along the developed surface of the fracture with a certain orientation towards the center.

The diversified electron-microscopic graphs and the various quantitative share of the mentioned aggregates suggest that the kind of glycol used for the synthesis of poly(ϵ-caprolactone) has an effect on the morphology and probably on the phase division of the appearing urethane elastomers. Considering the results given in Table III and those of the electron-microscopic observations, some reflections arise. The urethane elastomer which contains the rest of the decanediol in its structure (sample R-25) comparatively has the highest hardness and stiffness measured as the stresses at 50% and 100% elongation. Among the glycols used, it is decanediol that has the greatest length of carbon chains, and it was difficult to expect a higher stiffness of the normal chains, appearing at the macro scale in the form of high hardness and stiffness of the elastomer obtained. The electron-microscopic graph of the brittle fracture shows that this elastomer has spherulite and comparatively the highest content of dispersed phase structure. This suggests that the high hardness and stiffness of this elastomer follows from the considerable quantitative share of morphological forms in its structure. This conclusion is confirmed by the high hardness and stiffness of those urethane elastomers that contain ethanediol (sample R-23, Fig. 6) and pentanediol (sample R-24, Fig. 7) in their structure. These elastomers also have a considerable

content of the dispersed phase. Furthermore, we believe that the lower hardness and stiffness of urethane elastomers which have the rest of the diethylene glycol (sample R-28, Fig. 5) and butanediol (sample R-29, Fig. 4) in their structure follow from their slightly different morphology, characterized by presence of an interpenetrating phase structure or a minimum quantity of the dispersed phase. Thus, it should be concluded that previously obtained results on the influence of composition and preparation parameters[22-32] are in line with the findings of this work.

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