

Microphase Separation in Urethane Elastomers as Seen through NMR Measurements

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Synopsis

Urethane elastomers were prepared from poly(ethylene adipate) glycol or poly(tetramethyleneoxide) glycol, 4,4'-diphenylmethane diisocyanate, 1,4-butanediol, or 3,3'-dichloro-4,4'-diaminodiphenylmethane, or ethylenediamine as chain extenders. The glass transition of the polymers was determined from thermomechanical measurements. The essential conclusions were derived from pulsed NMR investigations. These made it possible to determine the extent of microphase separation, to evaluate the contribution due to the interface between the hard and soft domains, and to show that the glass transition itself may lead to ambiguous conclusions regarding the perfection of the separation. It was also suggested that the second moment can be related to the purity of hard domains.

INTRODUCTION

The excellent physical properties of urethane elastomers are now generally ascribed to microphase separation developing in these systems. As is known, the macromolecules of these elastomers are composed of flexible polyester or polyether segments of low glass transition temperature and of stiff urea or urethane blocks of high transition temperature. The incompatibility of the segments so different chemically leads to the microphase separation consisting in the formation of hard urea or urethane domains segregated from soft polyester or polyether matrix.¹⁻³ It is obvious that as complete as possible information on structure-property relations is necessary for proper design of these polymer systems. Such information can be extracted, e.g., from modulus-temperature relations.⁴ One of the most easily accessible methods of measuring the perfection of the separation are the measurements of changes in the glass transition temperature.⁵⁻⁸ Also, the thermodynamic analysis of the polymer-solvent interactions can give an insight into this question.⁹ Specially valuable seems to be quantitative information on the volume or weight fraction of the hard domains and on how important is the domain interface. This can be achieved by SAXS measurements.¹⁰⁻¹² Similar results can be obtained from pulsed NMR investigations.^{13,14} The utility of the latter technique stems from its sensitivity to the molecular dynamics of polymers. As is known, e.g., Refs. 15-17, when placed in a static magnetic field H_0 , the protons of the investigated sample undergo precession about the field direction and follow a Boltzmann distribution between the two energy states, with a slight excess of protons in the lower state relative to the upper one. This results in a small macroscopic magnetization along the field direction (z-direction). However, as a result of small variations in local magnetic fields, the spins do not precess at the same rate, in phase. This leads

to zero magnetization in the direction perpendicular to the direction of H_0 , i.e., in the x,y plane. Application in this plane of another field H_1 (which rotates at the same frequency as nuclear precession) tends to tip the macroscopic magnetization and makes the protons precess in phase. This produces a transverse magnetization rotating in the x,y plane, which is easy to detect with an appropriate coil. After the H_1 field is switched off, the return of the nuclear magnetization to equilibrium occurs, and the precessing spins tend to get out of phase. As a result, the transverse magnetization decays to zero. If the spins are placed in a relatively rigid lattice, then the local field seen by the nuclei is determined mainly by the interaction between the nuclei magnetic dipoles and varies greatly across the sample. The nuclear moments tend to get out of phase very quickly and the decay of magnetization can be approximated by the following equation:

$$\ln M_t = \ln M_0 - \frac{1}{2}\Delta H^2 t^2 \quad (1)$$

where M_t and M_0 stand for the magnetization after time t and at the beginning of the decay, respectively, and ΔH^2 is the so-called second moment expressed in the angular frequency units. If the nuclear spins possess a great deal of motion (e.g., macromolecules above the glass transition), then the spin-spin interaction is not so efficient, the nuclear moments get out of phase much slower, and the decay is described by the following equation:

$$\ln M_t = \ln M_0 - t/T_2 \quad (2)$$

where T_2 is the spin-spin relaxation time. Equation (1) corresponds to a broad Gaussian shape of the equivalent absorption line, whereas eq. (2) is equivalent to a narrow Lorentzian line.

Assink^{13,14} and Wilkes¹³ have shown that the microphase separation is seen in the magnetization decay and that the hard domains in the urethane elastomers are rigid enough to make the decay follow eq. (1), while the decay within the soft matrix is described by eq. (2). As a consequence, the second moments and relaxation times deliver some information on the respective phases and, since the magnetization at the beginning of the decays is proportional to the amount of protons in the respective phases, the degree of the separation can be relatively easily obtained. That is why it was decided to investigate by this technique, as a continuation of previous works from this laboratory,^{8,9,18} several polyurethanes of commercial importance.

EXPERIMENTAL

Materials

The polyurethane investigated in this work were prepared by a prepolymer method. The soft segment was either poly(ethylene adipate) (PEA) or poly(tetramethyleneoxide) (PTMO); the molecular weight was 2000 in both cases. All the polymers were based on 4,4'-diphenylmethane diisocyanate (MDI). 1,4-Butanediol (BDO) or 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) or ethylenediamine (EDA) were used as chain extenders. BDO- and MOCA-extended polyurethanes were synthesized in bulk. The prepolymer method consisted in drying the polyester under reduced pressure (385 K, 3 mm Hg, 2 h),

then the prepolymerization with MDI was carried out at 395 K for 30 min, and finally the chain extension with BDO or MOCA was achieved in a centrifuge at 395 K for 5–75 min and completed in an oven for 24 h at 395 K. The amount of hard segments was changed in two different ways. In the series designated BR-, different amounts of MDI were used for the prepolymerization reactions, so that the concentration of free NCO groups varied from one prepolymer to another (the molar ratios of NCO/OH during the prepolymerizations varied from 2.3 to 5.5). The synthesis of the polyurethanes designated BM- was modified so that only one prepolymer was obtained at the ratio of NCO/OH = 2.75 and then varying amounts of MDI were mixed with the prepolymer. In both series the stoichiometry during the chain extension was kept at NCO/OH or NCO/NH₂ equal to 1.1.

EDA extended polyurethanes were synthesized in solutions. The prepolymerization of PTMO with varying amounts of MDI were carried out in dried dioxane at 330 K for 6–8 h. Before the reaction PTMO was stripped of moisture and gas at 320 K for 30 min under vacuum of 3 mm Hg. The chain extension was carried out at 240 K in large excess of dimethyl formamide, so that the concentration of polymer in the final mixture was about 3–5%. Slow evaporation of the solvent produced polymer films that were dried to constant weight under vacuum at 330 K. This series of polymers is designated SR-.

In addition to the symbols, BR-, BM-, SR-, every polymer is identified by the

TABLE I
Molar Compositions of the Investigated Elastomers

Polymer	PEA	PTMO	MDI	EDA	MOCA	BDO
BR-G-25	1.0		2.35			1.14
BR-G-29	1.0		2.75			1.43
BR-G-35	1.0	x	3.50	x	x	2.08
BR-G-39	1.0		4.25			2.76
BR-G-44	1.0		5.00			3.57
BR-G-47	1.0		5.30			3.82
BR-A-33	1.0		2.31		1.09	
BR-A-36	1.0		2.59		1.36	
BR-A-42	1.0	x	3.01	x	1.72	x
BR-A-45	1.0		3.48		2.08	
BR-A-49	1.0		4.00		2.63	
BR-A-52	1.0		5.00		3.50	
BM-G-29	1.0		2.75			1.50
BM-G-35	1.0		3.50			2.19
BM-G-38	1.0	x	4.00	x	x	2.62
BM-G-41	1.0		4.50			3.11
BM-G-44	1.0		5.00			3.53
BM-A-35	1.0		2.75		1.48	
BM-A-40	1.0		3.30		1.97	
BM-A-46	1.0	x	4.00	x	2.61	x
BM-A-49	1.0		4.50		3.11	
BM-A-53	1.0		5.10		3.63	
SR-D-17		1.0	1.50	0.50		
SR-D-19		1.0	1.75	0.75		
SR-D-22	x	1.0	2.00	1.00	x	x
SR-D-23		1.0	2.15	1.15		
SR-D-25		1.0	2.30	1.30		

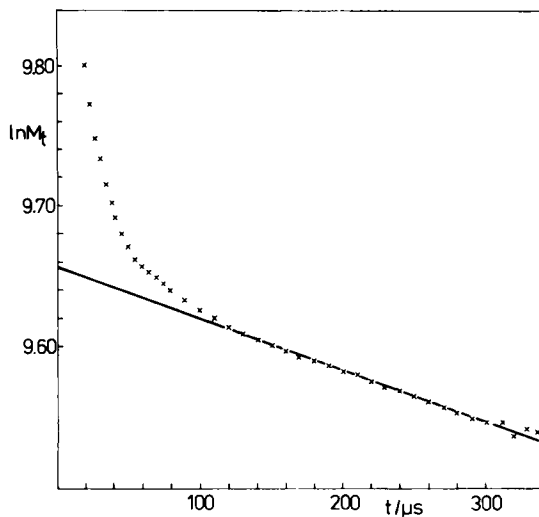


Fig. 1. The decay of magnetization of BM-G-35, M_t is given in arbitrary units.

nature of chain extender: A for MOCA, D for EDA, and G for BDO. The figure following the symbols indicates the weight fraction of hard segments in percent. The molar compositions of the investigated samples are given in Table I.

Measurements

The NMR measurements were performed by means of a Bruker-SXP 4-100 Spectrometer operating at 25.5 MHz in the phase sensitive detection mode. The transverse magnetization was produced with $\pi/2$ pulse of $2 \mu\text{s}$ length. The pulses were spaced 1 s apart. For every measurement 200 decays were collected by a Datalab DL 905 Transient Recorder and averaged by a Mera 400 Computer. All the measurements were performed at a room temperature.

The thermomechanical analysis was carried out in tension by means of a TMA-Politechnika Lodzka analyzer. The experimental details and the way in which the glass transition was determined are given in a previous paper.⁸

RESULTS AND DISCUSSION

Figures 1 and 2 show typical decays obtained in this work. The first initial component reflecting the existence of hard domains and the slow component corresponding to the soft matrix are clearly seen. It is also seen that for times longer than $120 \mu\text{s}$ for BM-G-35 and $45 \mu\text{s}$ for SR-D-17 the decays are well approximated by eq. (2). This approximation makes it possible to find the values of magnetization of the soft phase corresponding to the region where the fast decay takes place. In this way, from the initial sections of the curves, the values of the magnetization produced by protons in the rigid environment were isolated. The obtained values were subsequently approximated by eq. (1), which for SR-D-17 is presented in Figure 3. Similar results were obtained for other members of SR-D- series. In the case of BR- and BM- series, it was not, however, possible to approximate the initial values by one equation of the Gaussian type.

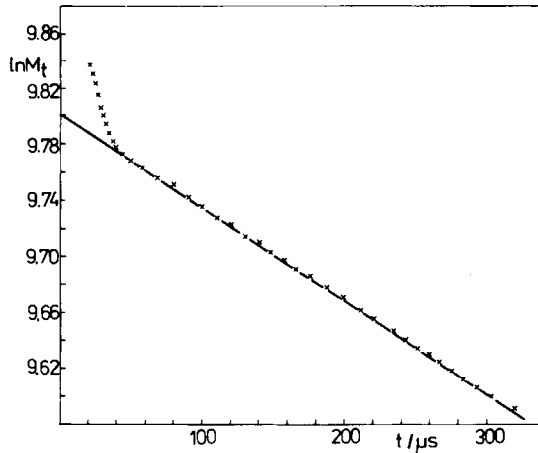


Fig. 2. The magnetization decay of SR-D-17, M_t is given in arbitrary units.

Instead, two fast components that are shown in Figures 4 and 5 were isolated for these elastomers.

Expressing these results in terms of the absorption line width, δH , one obtains that the decays approximated by eq. (2) correspond to Lorentzian curves with $\delta H \cong 0.01$ G, while the fast decays [eq. (1)] correspond to Gaussian curves with $\delta H \cong 1.3$ G (the slower component) and $\delta H \cong 5$ G (the faster component). While the faster of the Gaussian components is quite obviously due to the protons from the hard domains, the slower one might be ascribed to chemical crosslinking (allophanate or biuret bonding), to poorly developed crystallinity, or to an interface between the hard and soft domains. Since there is no indication of crystallinity as measured by WAXS and since there is no correlation between this component and the crosslinking,¹⁹ it was concluded that the slower of the Gaussian components reflects the interface between the domains. Within such an interface the molecular mobility should be intermediate between the mobility within the domains and produce signals of an intermediate width. As was mentioned above, SR-D- elastomers lack this interface component. It does not,

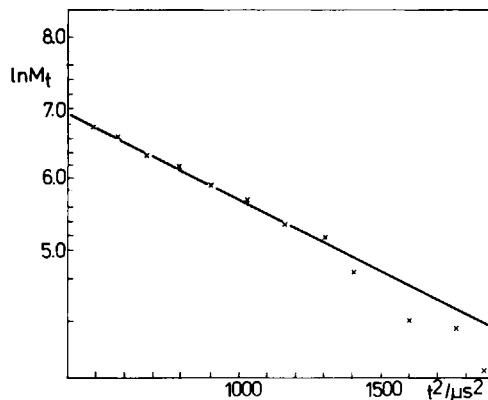


Fig. 3. Equation (1) behavior of the fast component of the decay for SR-D-17.

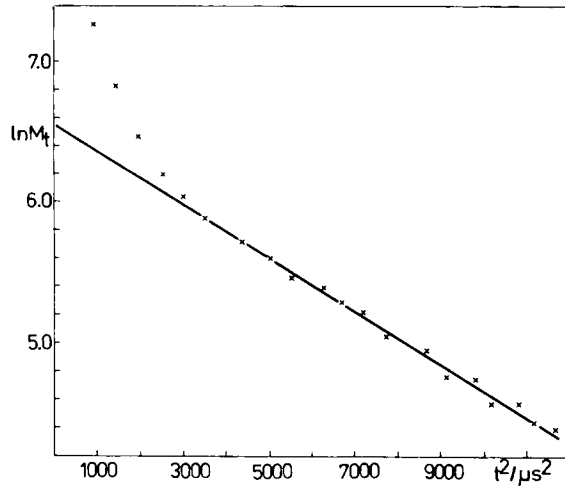


Fig. 4. The slower of the fast components for BM-G-35.

however, mean that the interface does not exist in the case of these elastomers. Most probably it is sharp enough not to be detectable with the applied technique. It is worth mentioning in this respect that Paik-Sung et al.²⁰ derive a similar conclusion from the IR spectra. To be sure, their polyurethanes differed from the ones investigated here in that 2,4-toluene diisocyanate was used instead of MDI, but the authors relate the high perfection of the separation rather to the nature of the chain extender than to the diisocyanate. With the more symmetric MDI the perfection of the separation may be expected to be even better. The sharp interface may also be partly due to the preparation technique. SR-D-polyurethanes were solution polymerized and the kinetic factors during evaporation are certainly more favorable to formation of better segregated phases than in the case of bulk polymerized systems.

Extrapolation to $t = 0$ enables to obtain M_0 for all these components and to calculate the fraction of the material that is engaged in the interface formation.

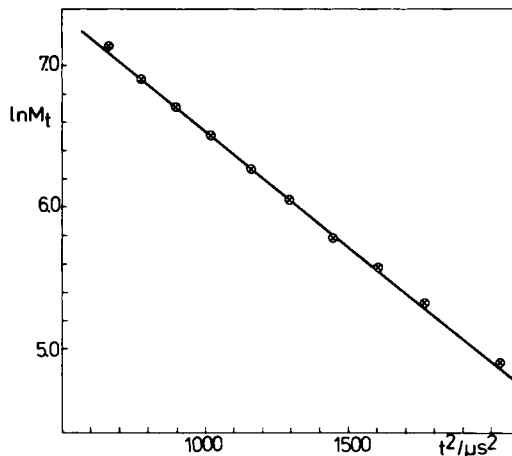


Fig. 5. The faster of the fast components for BM-G-35.

TABLE II
The Characteristics of Domain Interface

Polymer	w_i^a (%)	ΔH_{2i}^2	Polymer	w_i^a (%)	ΔH_{2i}^2
BR-G-25	2.6	0.48	BR-A-33	2.9	0.52
BR-G-29	3.6	0.51	BR-A-36	3.3	0.47
BR-G-35	4.7	0.53	BR-A-42	4.1	0.49
BR-G-39	5.8	0.47	BR-A-45	5.5	0.53
BR-G-44	7.5	0.50	BR-A-49	5.9	0.46
BR-G-47	8.1	0.49	BR-A-52	6.2	0.51
BM-G-29	2.8	0.55	BM-A-35	3.2	0.59
BM-G-35	4.4	0.59	BM-A-40	2.9	0.51
BM-G-38	4.1	0.55	BM-A-46	3.5	0.51
BM-G-41	3.9	0.53	BM-A-49	3.2	0.48
BM-G-44	4.4	0.53	BM-A-53	3.2	0.49

^a w_i is the weight fraction of the material involved in the interface formation in percent; ΔH_{2i}^2 is the second moment of interface protons (expressed in G²).

These data, together with the second moments, are collected in Table II.

Analyzing the data in the above table it should be noted that the weight fraction of the material involved in the interface formation is approximately constant within the investigated composition range for BM-G- and BM-A- series. In the case of BR-G- and BR-A- series the fraction appears to increase with the ratio of NCO/OH at the prepolymer formation. This trend is seen clearer for BR-G-elastomers than for BR-A- series.

The polymers from BR- and BM- series differ only in that the molecular weight distribution of oligomeric molecules in the prepolymer is the same for the elastomers belonging to BM- series while within BR- group it is variable, i.e., the higher the ratio of NCO/OH, the smaller the contribution of oligomers of higher polymerization degree.²¹⁻²³ Thus, the distribution of the polymerization degrees seems to be responsible for the variation within BR- series, so that greater polymerization degrees of prepolymer molecules favor formation of narrower transition zone between the domains. Such a result may be taken as one more reflection of the thermodynamic prediction²⁴ that longer segments lead to better separation. In other words, it seems to be more proper to consider the soft

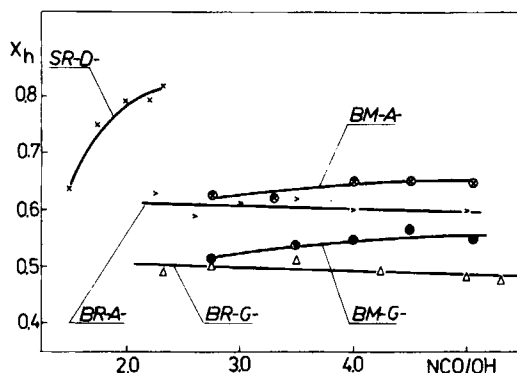


Fig. 6. Changes in the perfection of microphase separation in the investigated systems. X_h is the ratio of the material aggregated into hard domains to the total amount of hard segments present in the systems; NCO/OH refers to the prepolymerization step.

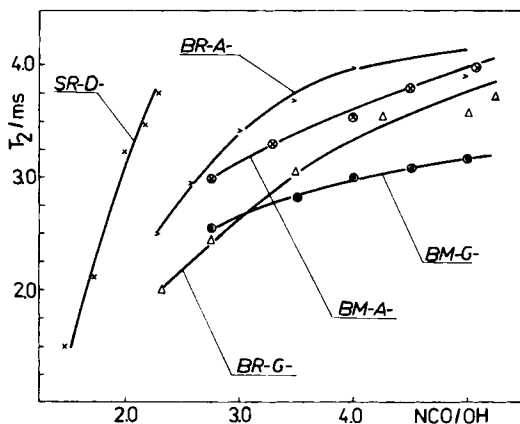


Fig. 7. The spin-spin relaxation times for the investigated systems.

segments to be not PEA blocks alone but entities such as PEA-MDI-PEA, PEA-MDI-PEA-MDI-PEA, etc.

The amount of the material that is aggregated into hard domains (as measured by NMR) can be compared to the total amount of the hard segments (MDI + BDO or MDI + MOCA or MDI + EDA) present in the investigated systems. The ratio of these quantities, X_h , can be taken as the most direct measure of the perfection of separation. The X_h results are collected in Figure 6. In the light of what has been said about MDI units connecting the polyester blocks, it would be more appropriate to compare the amount of hard domain material with the total amount of hard segments diminished by this part of MDI that serves as these connecting units. Such calculations require, however, precise knowledge of the hard segment statistics which is not known. Assuming the validity of Flory distribution one finds that the slopes shown in Figure 6 are slightly changed, but the relations between the series are preserved. This correction was not, however, taken into account because it is not sure whether these statistics—or deviations from it—apply in the same extent to all the polymers studied. There is one more reason not to correct the basis of X_h calculations. As will be discussed later, the hard domains most probably contain an amount of soft segments that also contribute to the NMR signal. Thus, $X_h = 1$ does not necessarily mean that all the hard segments are aggregated into domains. Keeping all these reservations in mind one can see from Figure 6 that the perfection of the separation rapidly increases within SR-D- series. Because of the fast decreasing solubility of these elastomers, it was not possible to prepare samples of higher isocyanate content. The trend seen in this figure suggests, however, that at the contents corresponding to the other investigated series the perfection may be quite close to the ideal one, the more so as the values of T_g of the soft segment phase tend to approach the value of the free soft segment if NCO/OH is increased. Also, as follows from Figure 7, parallel to X_h run the spin-spin relaxation times of the soft phase. This certainly reflects increasing molecular mobility within this phase, which means that the amount of solubilized hard segment is progressively smaller if the urea content is increased. The above mentioned T_g values change from 220 K for SR-D-17 to 203 K for SR-D-25 while the glass transition of PTMO segment is about 185 K.

In contrast to SR-D- series, the other investigated polymers exhibit much poorer separation of the segments. It is seen, however, that the microphase separation is always better in MOCA based elastomers if compared with BDO extended systems. Also, BM-G- and BM-A- polymers are better separated than their BR- analogs. Apparently, the molecular weight distribution of prepolymer affects not only the interface but also the hard domain formation. The polymers from BR- and BM- series differ from those belonging to SR-D- series also in that X_h is rather insensitive to changes in the composition ratio. This result was rather unexpected, since it was found that the glass transition temperature of the soft segment phase progressively increases from 240 K for BR-G-25 to 252 K for BR-G-47 and from 242 K for BR-A-33 to 248 K for BR-A-52. As far as BM-G- and BM-A- polymers are concerned, the glass transition does not seem to be influenced by the composition ratio and is about 246 K for BM-A- and 247 K for BM-G- polyurethanes. These variations in the glass transition suggest that for BR-G- and BR-A- elastomers the perfection of the separation depends very clearly on the composition (in a more quantitative way this reasoning was presented in a previous paper⁸). Thus, the NMR results appear to be in contradiction to the glass transition data. This contradiction may be resolved if one takes into account that the mobility of soft segment, which determines its glass transition, is restricted not only by the hard segments dispersed in the soft phase but also by anchoring both segment ends to the hard domains. This anchoring effect obviously depends on how sharp is the interface. If this interface is sharp, as it seems to be in the case of SR-D- polyurethanes, the glass transition is controlled mainly by the solubilized hard segments. However, if the interface is diffuse, the anchoring reduces the mobility to a significantly greater extent because of penetration of the soft segments into the hard material that is involved in the interface formation.²⁵ Apparently, this effect is the predominant one in the case of BR-G- and BR-A- polymers. In fact, the amount of the solubilized hard segments seems to be even decreased with increase in NCO/OH ratio, as is seen from the changes in the spin-spin relaxation time (Fig. 7). From the way the NMR data were processed, it should be clear that the spin-spin relaxation times are derived from the soft phase behavior only, without taking into account the mobility within interface, while the thermomechanical measurements in tension make allowances for the mobility within the interface. It should be also noted that for BM-G- and BM-A- elastomers the stable glass transition temperatures within these series are accompanied by approximately the same amount of the interface material. The latter fact reinforces the above reasoning concerning the relation between the glass transition and the anchoring effect. Thus, a drop in the glass transition temperature within a series of polyurethanes means an improvement in the perfection of the separation; it does not, however, unequivocally point to whether this improvement is achieved by a decrease in the amount of solubilized hard segments or by producing a sharper interface. Pulsed NMR measurements are in this respect more instructive.

As seen from Figure 7, the spin-spin relaxation time is always longer for MOCA based elastomers than for BDO analogs. It means that the soft polyester phase is purer in the case of the amine extender than in the case of glycol one. Also, the spin-spin relaxation time for BM-G- polyurethanes are shorter than for BR-G- analogs. Similar relation is observed for BM-A- and BR-A- elastomers. These relations may be explained if one recalls that the average polymerization

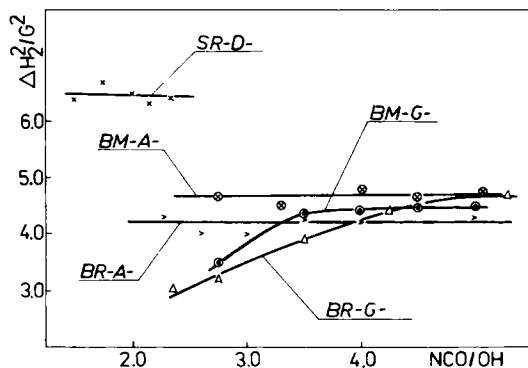


Fig. 8. The second moment vs. NCO/OH ratio for the investigated series.

degree at the prepolymerization stage is—on average—greater for BM- series than for BR- ones. In other words, there are more MDI units connecting PEA segments in the soft polyester phase in, e.g., BM-A-49 than in BR-A-49. These MDI units impose certainly some restriction on the molecular mobility and may be taken as an explanation of the shorter T_2 in the polymers belonging to BM-series.

In Figure 8 the second moments of the hard domain protons, calculated by means of eq. (1), are presented. Before the results are discussed it should be recalled that the second moment ΔH_2^2 , of a number of protons in a rigid isotropic material depends on Σr_{jk}^{-6} , where r_{jk} is the length of the vector joining proton j and k .¹⁵ The effect of molecular motion can be seen as a reduction in the second moment since the time average of r_{jk} enters the equation on the second moment. It must be also remembered that this reduction is observed when the frequency of motion exceeds the width of the absorption line measured in frequency units. For typical glassy polymers the second moment is about 15–25 G² (e.g., Ref. 15). The hard domains in the investigated polymers are also glassy. Thus, the values presented in Figure 8 might be expected to be close, or even within, the above-mentioned range. It is not, however, the case. The values shown in Figure 8 fall in the range of 3–6 G². It is equivalent to saying that quite effective molecular motion takes place within the domains. The most reasonable explanation of the fact is to allow for inclusion of some soft segments into the hard domains. Such a possibility has been already taken into account by other investigators to explain changes in the glass transition of hard domains (e.g., Ref. 7). The solubilized soft segments acting as a sort of plasticizer facilitate localized motions within the domains. If such an explanation of the relatively small ΔH_2^2 values is accepted, then it must be concluded from the data presented in Figure 8 that the composition ratio does not affect the hard domain structure in the case of all systems based on the diamine extenders, i.e., the concentration of the soft segments dissolved in the hard domains is not essentially changed. An exception to this are BDO-extended polyurethanes. In this case a decrease in molecular motion is seen with increase of NCO/OH, as if the concentration of the soft segments was decreased in the domains built from longer urethane blocks. One can also note that ΔH_2^2 for BR-G- series is always smaller than for BM-G- one. As has been already pointed out, the average polymerization degree of prepolymer molecules is greater in the case of BM-G- polyurethanes, which certainly

makes the inclusion of the soft segments less probable and the hard domains purer.

The glass transition temperatures of the hard domains increase essentially with NCO/OH ratio for all the investigated systems, i.e., from 438–453 K within the SR-D- series and from 406–421 K within BDO-extended polymers. For MOCA-extended elastomers the glass transition was beyond the operation range of the TMA instrument, but from modulus–temperature behavior⁹ it is seen that the trend should be similar to the ones observed for BDO polyurethanes. All these glass transition data might suggest that for the investigated systems the purity of the hard domains is remarkably improved if NCO/OH is increased. Such a conclusion is not, however, in line with ΔH_2^2 findings. The glass transition itself may also in this case lead to uncorrect conclusions. Considering, e.g., two polymers obtained at NCO/OH = 3 and NCO/OH = 5, one may calculate²² that the average hard segment molecular weights are 930 and 1610, respectively, if the hard segments are formed from MDI and BDO. Such an increase in the molecular weight itself certainly elevates the glass transition temperature. Thus, the changes in the glass transition of hard domains seem to be not sufficient to draw conclusions regarding the purity of the domains.

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