Macromolecules **1995**, *28*, 3739−3740

Enhancement of Orientational Coupling in Bidisperse Polybutadiene Melts through the Implementation of Directed Interactions

Ulf Seidel and Reimund Stadler*

Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, Becherweg 18–20, 55099 Mainz, Germany

Gerald G. Fuller

Department of Chemical Engineering, Stanford University, Stanford, California 94305-5025

Received November 28, 1994
Revised Manuscript Received March 3, 1995

For the modeling of chain dynamics in binary polymer melts, it has been found that, in addition to reptational motion,[1] the effects of constraint release[2−5] and orientational coupling[6−8] need to be considered. Orientational coupling is the presence of segmental orientation of short chains after the release of macroscopic stress imposed on this species. In a recent paper,[9] we reported a study of the relaxation behavior of bidisperse temporary networks using simultaneous measurement of IR birefringence and dichroism. Chemical moieties capable of forming binary hydrogen bond complexes (phenylurazole units, PU; Figure 1) were attached randomly, and the orientational coupling coefficient ϵ[9,12] became a function of temperature and sample composition (which is not the case in simple miscible binary blends[6,8]).

Thus, orientational coupling may be described as a sum of two contributions, one of them being the intrinsic coupling also found in other binary blends (which is a function of neither temperature nor sample composition) and the other being attributed to the binary interchain complexes which are formed by the interaction of PU groups.

To further explore this phenomenon, samples with higher fractions of stickers were prepared in order to establish a relation between the numbers of stickers per chain and the coupling coefficient.

Materials and Methods

A detailed description of the rheooptical technique has been published.[10] The polybutadienes, their chemical modification, composition of the binary mixtures, and the experimental procedure are identical to the ones reported[9] except that samples with degrees of modification of 2, 3, and 4% were investigated here (e.g., 2, 3, and 4% of the repeating units bearing urazole groups, respectively). The terminal relaxation times of the single blend components at the two experimental temperatures are listed in Table 1.[11]

In all experiments, data were collected for 10 s and normalized to the first data point after the strain step. For the determination of the coupling coefficient, ϵ, only the data points collected well after complete relaxation of the pure short component were taken into account.

Results and Discussion

The orientational coupling coefficients ϵ, as obtained by the graphical determination method described earlier,[9,12] are listed in Table 2. Each value represents a mean of six to eight independent experiments. The experimental errors of these mean values are smaller than ±0.05. For comparison, the results for 1% modification taken from previous work[9] are included.

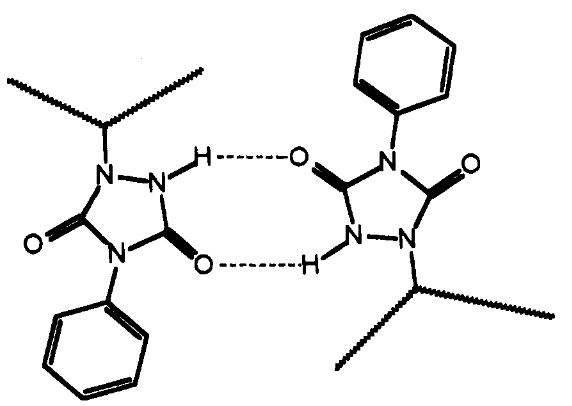

Figure 1. Formation of hydrogen bonds between urazole units.

Table 1. Terminal Relaxation Times of the Single-Blend Components at the Two Experimental Procedures (PB*xy*−PU*z*; *xy* Indicates Molecular Weight × 1000, *z* Indicates Percentage of Repeating Units Bearing Stickers; in dPB*xy*, 70% of the CH_2 Groups Are Deuterated)

polymer	τ_d at −2 °C (s)	τ_d at −20 °C (s)
PB28−PU1/dPB29−PU1	0.1	2
PB28−PU2/dPB29−PU2	0.25	2.5
PB28−PU3/dPB29−PU3	0.45	3.5
PB28−PU4/dPB29−PU4	1.5	5
PB109−PU1,2,3,4	≥50	≥500

Table 2. Orientational Coupling Coefficients for PB109−PU/PB28−PU Blends at Different Degrees of Modification, Temperatures, and Sample Compositions

PB109/	1% PU		2% PU		3% PU		4% PU	
PB28 (%)	−2 °C	−20 °C	−2 °C	−20 °C	−2 °C	−20 °C	−2 °C	−20 °C
70/30	0.70	0.72	0.70	0.81	0.84	0.97	0.87	0.97
50/50	0.66	0.70	0.69	0.76	0.81	0.92	0.84	1.0
30/70	0.60	0.64	0.61	0.68	0.68	0.76	0.76	1.01

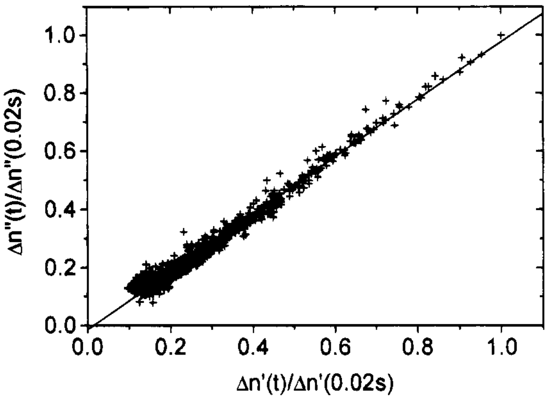

Figure 2. Determination of ϵ for PB109−PU4/PB28−PU4 50/50 at −20 °C (the straight line represents the linear regression of the data points in order to obtain ϵ).

The data agree with our previous finding that the polar stickers increase orientational coupling. In addition, the increase in ϵ for increasing fraction of long chains has been reconfirmed as well as the increase in ϵ with decreasing temperature. Therefore, the proposed relationship $\epsilon = \epsilon_{\text{intrinsic}} + \epsilon_{\text{excess}}$[13] seems to be valid. Furthermore, the data listed in the table show a significant dependence on the degree of modification (e.g., the number of stickers per chain). This dependence leads up to the coupling coefficient of 1 for 4% modification at −20 °C, indicating complete coupling of segmental orientation of the short-chain species (probe) to the segmental orientation of the long-chain species

0024-9297/95/2228-3739$09.00/0

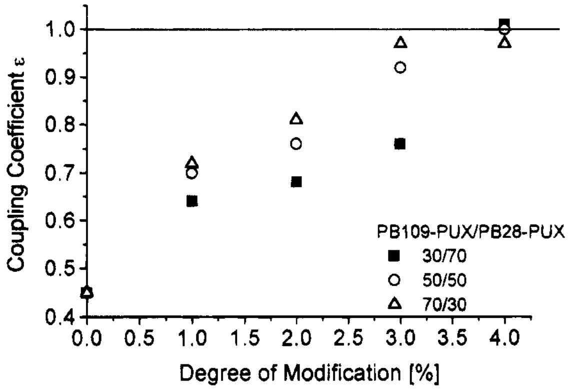

Figure 3. Orientational coupling coefficients versus degree of modification at −20 °C (the line at $\epsilon = 1$ represents complete coupling of the segmental orientation of the probe to that of the matrix; x = degree of modification).

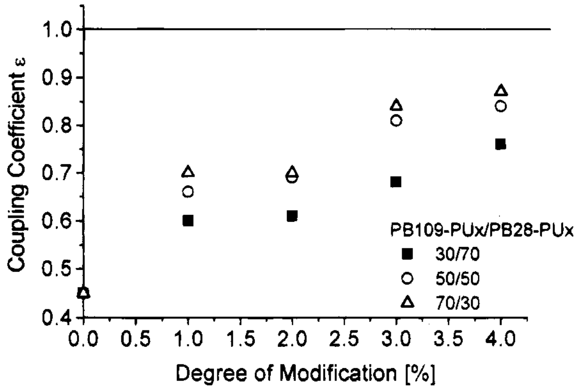

Figure 4. Orientational coupling coefficients versus degree of modification at −2 °C (the line at $\epsilon = 1$ represents complete coupling of segmental orientation of the probe to that of the matrix; x = degree of modification).

(matrix). A typical example for this is shown in Figure 2.

Figures 3 and 4 show plots of the orientational coupling coefficient versus degree of modification for −20 and −2 °C, respectively. A line at $\epsilon = 1$ indicates complete coupling.

These plots together with results of Ylitalo et al.,[14] Jacobi et al.,[15] and Sotta et al.[16] may lead to a possible explanation of the nature of the observed increase in orientational coupling. In the cited publications,[14−16] the authors independently found coupling coefficients of $\epsilon = 1$ for different systems whenever the shorter species in their bimodal samples was below the entanglement molecular weight (M_e). Ylitalo et al.[14] found that the coupling coefficient then decreases as soon as the molecular weight of the shorter component is close to the entanglement molecular weight and then reaches a final value independent of the molecular weight as both chain species are longer than M_e. This result is important for the interpretation of our data. The polybutadiene components used in this study (M_w = 109 000 and M_w = 28 000) are both well above the entanglement molecular weight for 1,4-polybutadiene ($M_e \approx 1900^{17}$). IR spectroscopy demonstrated that only a certain percentage of urazole groups is incorporated in binary hydrogen bond complexes. From the IR data (taken at 20−100 °C) the fraction of polar stickers which is not included in complexes may be estimated to be 0.21 at −20 °C. At about 3.3% modification of the polybutadiene chains there is one bound urazole group (and thus one effective contact) per entanglement spacing on average. Figure 3 shows that this is exactly the lowest degree of modification where a coupling coefficient of $\epsilon = 1$ would be obtianed. This demonstrates that with one effective interchain contact per entanglement the same degree of coupling, as is the case of oligomers in entangled matrices, is present.

Acknowledgment. G.G.F. thanks the NSF for support through Grant DMR 9120360. U.S. gratefully acknowledges financial aid from the Fonds der Chemischen Industrie (FdCh), the "Graduiertenkolleg Chemie und Physik superamolekularer Systeme", "Deutsche Kautschukgesellschaft".

References and Notes

(1) Doi, M.; Edwards, S. F. *The theory of polymer dynamics*; Clarendon: Oxford, U.K.
(2) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *42*, 67.
(3) Rubinstein, M.; Colby, R. H. *J. Chem. Phys.* **1988**, *89*, 5291.
(4) Rubinstein, M.; Helfand, E.; Pearson, D. S. *Macromolecules* **1987**, *20*, 822.
(5) des Cloizeaux, J. *Macromolecules* **1990**, *23*, 4678.
(6) Doi, M.; Pearson, D.; Kornfield, J.; Fuller, G. G. *Macromolecules* **1989**, *22*, 1488.
(7) Merrill, W. W.; Tirrell, M.; Jarry, J.-P.; Monnerie, L. *Macromolecules* **1989**, *22*, 896.
(8) Watanabe, H.; Kotaka, T.; Tirrell, M. *Macromolecules* **1991**, *24*, 201.
(9) Seidel, U.; Stadler, R.; Fuller, G. G. *Macromolecules* **1994**, *27*, 2066.
(10) Ylitalo, C. M.; Kornfield, J. A.; Fuller, G. G.; Pearson, D. S.
(11) For an explanation of the sample notations, see ref 9.
(12) Kornfield, J. A.; Fuller, G. G.; Pearson, D. S. *Macromolecules* **1989**, *22*, 1334.
(13) $\epsilon_{\text{intrinsic}}$ = coupling coefficient found for bimodal polybutadiene melts[14] (0.45). ϵ_{excess} = excess contribution to the coupling coefficient due to urazole−urazole complexes.
(14) Ylitalo, C. M.; Zawada, J. A.; Fuller, G. G.; Abetz, V.; Stadler, R. *Polymer* **1992**, *33* (14), 2949.
(15) Jacobi, M. M. Doctoral Dissertation, Freiburg University, Freiburg, Germany, 1989.
(16) Sotta, P.; Deloche, B.; Herz, J.; Lapp, A.; Durand, D.; Rabadeux, J.-C. *Macromolecules* **1987**, *20*, 2769.
(17) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(18) de Lucca Freitas, L.; Auschra, C.; Abetz, V.; Stadler, R. *Colloid Polym. Sci.* **1991**, *269*, 566.

MA946174G