ethylene. The equilibrium covers only the T(+) to T(−) equilibrium.[7] For PVF2 and P3FE successions of conformational disordering with relatively small energy differences are possible. Nothing seems to be known about possible conformational disorder in PVF.

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Registry No. PVF2, 24937-79-9; P3FE, 24980-67-4.

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Thermoplastic Elastomers by Hydrogen Bonding. 3. Interrelations between Molecular Parameters and Rheological Properties

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ABSTRACT: The properties of polybutadienes of narrow molecular weight distribution are modified by hydrogen bond interaction between 4-phenyl-1,2,4-triazolidine-3,5-dione (urazole) groups attached to the polymer backbone. The rheological properties of the modified polybutadienes are investigated as a function of the molecular weight and the degree of modification. The relaxation time spectra, obtained from the measured complex modulus G^*, are used to discuss changes in the rheological behavior. A broadening of the rubbery plateau zone and an increase of zero-shear viscosity and steady-state recoverable compliance J_e^0 are observed with increasing content of polar units. The hydrogen bonds between urazole units form a thermoreversible network. Due to the labile hydrogen bond linkages no rubber elastic equilibrium network modulus is observed in these systems.

Introduction

Thermoplastic elastomers are materials having properties similar to cross-linked rubbers at room temperature. At higher temperatures these materials are processable by common techniques convenient for thermoplastic materials. Generally two types of synthetic thermoplastic elastomers (TPE's) have been recognized. The first type includes SBS triblock copolymers and segmented block copolymers of the polyether–ester and polyether–urethane type. In these systems phase separation into a soft matrix and a rigid dispersed phase is responsible for the network structure. The hard-phase domains act as mechanical filler and multifunctional cross-links. The second type of thermoplastic elastomers is based on one-phase structures. The thermoreversible junctions are introduced by relatively weak interactions, which break at higher temperatures. The sulfonated EPDM's may serve as an example for this latter type.[1,2] In these systems thermoreversible cross-linking is achieved by the formation of aggregates of ionic dipoles. Until now the influence of the aggregate size on the final properties has not been studied in detail. Theoretical attempts to describe the viscosity and the dynamic behavior of ionomers assume the formation of dimeric aggregates.[3,4] Recent investigations on ionomeric model systems show that the number of associated dipoles may be larger than previously believed.[5] Another type of secondary valence interaction, capable of forming thermoreversible networks, is hydrogen bonds. This type of interaction is present in many biopolymer gels.[6] In contrast to the nondirected electrostatic interaction between ion dipoles, hydrogen bonds are oriented. In most cases only two distinct partners are involved in a hydrogen bond.

In order to investigate the complex phenomena associated with the formation and the properties of thermo-

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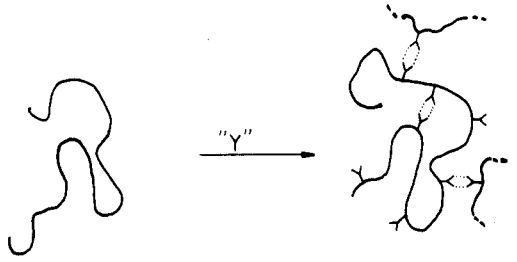
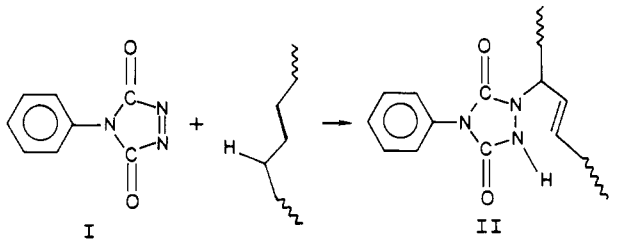


Figure 1. Schematical representation of the introduction of specifically interacting groups to a linear polymer.

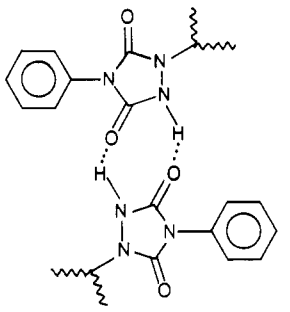
reversible networks a special type of model system has been prepared: the basic idea is to attach a defined number of specifically interacting groups to a nonpolar polymer backbone (Figure 1). In a previous paper[7] some preliminary results on the rheological behavior of thermoplastic elastomers based on hydrogen bond junctions have been reported. The temperature- as well as the time-dependent modulus has been discussed.

The functional groups forming hydrogen bonds were introduced by reacting diene rubbers (polybutadiene, polyisoprene, butyl rubber, EPDM) with 4-phenyl-1,2,4-triazoline-3,5-dione[8-10] (I).



I II

The resulting urazole groups (II) form hydrogen bond complexes (III) which may be characterized by IR spectroscopy.[11,12]



III

In the present paper a more detailed mechanical characterization of such modified polybutadienes in the linear viscoelastic region is given. The molecular weight dependence as well as the dependence on the number of interacting urazole groups will be considered.

Special emphasis will be given to the question of whether thermoplastic elastomers, based on a small number of interacting groups, show equilibrium network properties. In the preceding paper[7] it has been stated that the observed increase in the temperature-dependent storage modulus mainly reflects changes in the relaxation behavior. It is the main purpose of this paper to show that no equilibrium network modulus exists in thermoreversible networks of this type, but that the plateau modulus is altered due to the formation of a thermoreversible network structure. This may have some interesting consequences for the classification of network structures.

Theory

Due to the fact that the viscoelastic properties of polymers are strongly influenced by molecular weight distribution, polybutadienes with narrow molecular weight distributions were used as starting materials (see Experimental Section).

The important mechanical quantities characterizing the properties of polymer melts are obtained from the measured dynamic shear modulus

$$G^* = G' + iG'' \tag{1}$$

The steady-state viscosity at zero-shear rate, η_0, is obtained according to

$$\eta_0 = \lim_{\omega \to 0} G''(\omega)/\omega \tag{2}$$

While the viscosity is very sensitive to the molecular weight of entangled polymer melts, the steady-state recoverable compliance, J_e^0, is strongly affected by molecular weight distribution.[13]

J_e^0 is obtained from the measured quantities according to

$$J_e^0 = \lim_{\omega \to 0} G'(\omega)/|G^*(\omega)|^2 \tag{3}$$

Alternatively, the relaxation time spectrum $H(\tau)$ can be used to express the mechanical response of polymer melts and solids. Various approximations can be used to derive $H(\tau)$ from the quantities obtained by experiment. In the present work the second-order approximations derived by Tschoegl[14] are used.

For the more commonly used log–log representation the equations are

$$H(\tau) = G'[(\mathrm{d} \log G'/\mathrm{d} \log \omega) - \tfrac{1}{2}(\mathrm{d} \log G'/\mathrm{d} \log \omega)^2 + (1/4.606)(\mathrm{d}^2 \log G'/\mathrm{d}(\log \omega)^2)] \qquad 1/\omega = \tau/2^{1/2} \tag{4}$$

$$H(\tau) = (2G''/\pi)[1 - \tfrac{4}{3}(\mathrm{d} \log G''/\mathrm{d} \log \omega) + \tfrac{1}{3}(\mathrm{d} \log G''/\mathrm{d} \log \omega)^2 + (1/6.909)(\mathrm{d}^2 \log G''/\mathrm{d}(\log \omega)^2)] \qquad 1/\omega = \tau/5^{1/2} \tag{5}$$

The comparison of $H(\tau)$ derived from G' and G'' may provide a crucial test for the quality of the approximative formulas.

G'' and G' on the other hand are obtained by integral inversion from $H(\tau)$. The loss modulus is obtained according to

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\tau)\omega\tau/(1 + \omega^2\tau^2)\ \mathrm{d} \ln \tau \tag{6}$$

For viscoelastic liquids the storage modulus is given by

$$G'(\omega) = \int_{-\infty}^{+\infty} H(\tau)\omega^2\tau^2/(1 + \omega^2\tau^2)\ \mathrm{d} \ln \tau \tag{7}$$

while for viscoelastic solids, like a polymer network, a frequency-independent contribution of the network to the modulus must be taken into account

$$G'(\omega) = G_e + \int_{-\infty}^{+\infty} H(\tau)\omega^2\tau^2/(1 + \omega^2\tau^2)\ \mathrm{d} \ln \tau \tag{8}$$

Equations 4–8 provide the framework for answering the question of whether thermoplastic elastomers form networks, characterized by an equilibrium network modulus, or whether these systems are only a special type of transient network, like entangled polymer melts.

This procedure has been used for covalently cross-linked networks[15] applying different methods for the estimation of $H(\tau)$. A similar procedure was applied to SBS block copolymers for stress relaxation experiments.[16]

In a first step $H(\tau)$ is calculated from G' and/or G'' according to eq 4 and 5. From these equations $H(\tau)$ is

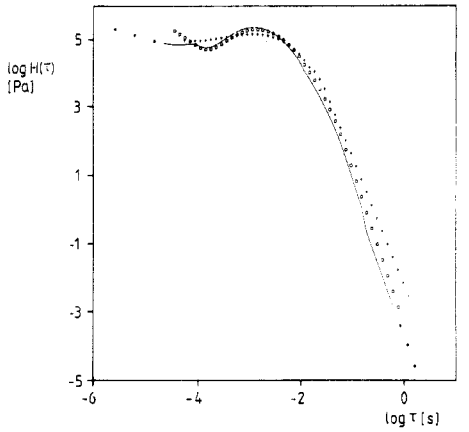


Figure 2. Calculated relaxation time spectra $H(\tau)$ of a linear polybutadiene melt (PB-26-0) in the terminal zone: (○) spectrum calculated according to eq 4 from G'; (+) spectrum calculated according to eq 5 from G''; (full line) spectrum after iterative optimization.

available from the experimental viscoelastic data only in a limited time span.

On the other hand, calculation of G' and G'' requires integration in the range from $-\infty$ to $+\infty$ (eq 6–8), but only relaxations with times in the same order of magnitude and longer than $1/\omega$ contribute to the modulus at a certain frequency. Faster relaxation processes with $\tau \ll 1/\omega$ do not contribute to the modulus. Thus the relaxation time spectrum obtained experimentally has to be expanded in the short time region for only about one decade, depending on the size of $H(\tau)$. On the other hand, the expansion to long relaxation time can be performed quite precisely by linear extrapolation of the terminal region.

For relaxation times $\tau \gg 1/\omega_m$, where ω_m is the frequency of the loss modulus maximum, $H(\tau)$ decays rapidly in linear polymer melts. As a consequence the contribution of these processes to the modulus becomes negligible.

The quality of the approximations of $H(\tau)$ from eq 4 and 5 can also be tested by calculating the loss modulus according to eq 6. In general both approximations of $H(\tau)$, starting either from G' or G'', give a reasonable description of G''. In most cases the deviations reflect difficulties in representing the experimental data by an analytical function for calculating the derivatives in a simple way. Thus the second derivative is especially subject to error. The approximate spectra can be optimized using an iterative method until a good fit of the calculated and the experimental loss modulus data is obtained. The details of the computational procedure will be given elsewhere.[17] A similar calculation was developed by Graessley.[18]

In Figure 2 the approximate spectra starting from G' and G'' as well as the final spectrum, obtained from the iterative procedure, are shown for a polybutadiene of molecular weight 26 000. In general we found that the final spectrum is very similar to the approximate spectrum obtained from G', while the spectrum obtained from G'' is more flat.

Using the optimized spectrum G'' and G' are calculated according to eq 6 and 7. In Figure 3 the experimental data as well as the calculated curve for G' and G'' are shown. The calculated and the experimental data fit very well. As expected, no equilibrium modulus is present in the polybutadiene melt. As will be discussed below, this procedure is used to decide whether an equilibrium modulus exists in the hydrogen bond networks or not.

It is of interest to compare the results obtained for a polymer with few interacting functional groups with these of the unmodified sample. The most detailed experimental

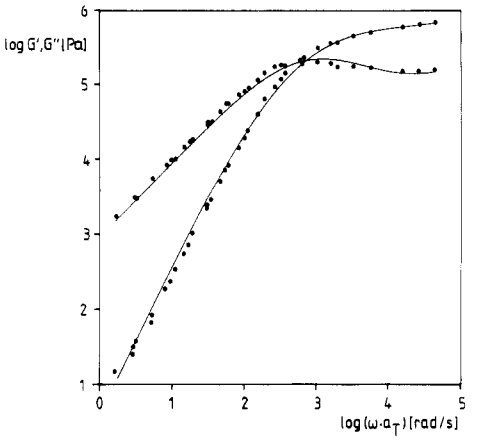


Figure 3. Storage and loss modulus G' and G'' of an entangled polybutadiene melt (PB-26-0); full lines are calculated from the optimized spectrum of Figure 2 according to eq 7 and 6.

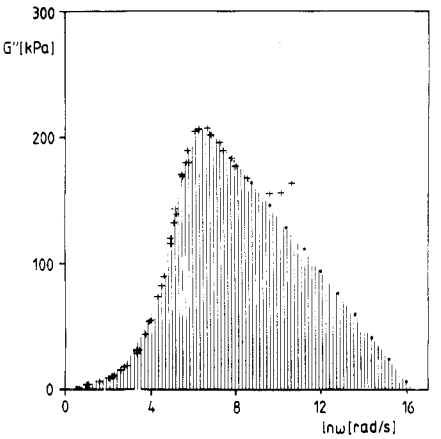


Figure 4. Semilogarithmic plot of the loss modulus (PB-26-0) G''; the shaded area corresponds to the terminal zone. G_N^0 is calculated from this area according to eq 11.

work on the rheological behavior in the terminal zone for polybutadienes of narrow molecular weight distribution has been performed by Graessley et al.[19,20] In the plateau and terminal zones the general behavior of the stress relaxation modulus is observed to follow the relationship

$$G(t) = G_N^0 U(t/\tau_0) \tag{9}$$

where G_N^0 is the plateau modulus, $U(t/\tau_0)$ is a universal decay function, and τ_0 is a characteristic time

$$\tau_0 = \eta_0 J_e^0 \tag{10}$$

The relaxation time spectrum $H(\tau)$ of the narrow distributed polymers is quite narrow and—as a consequence—a well-defined maximum in the loss modulus is observed.

For linear polymers of narrow molecular weight distribution, the dimensionless products $\omega_m \tau_0 \sim 2$ and $J_e^0 G_N^0$ appear to be universal constants.[21]

In general the plateau modulus, G_N^0, is given by

$$G_N^0 = 2/\pi \int_{-\infty}^{+\infty} G''(\omega)\, \mathrm{d} \ln \omega \tag{11}$$

where $G''(\omega)$ is the loss modulus of the terminal zone only. To calculate the plateau modulus according to eq 11 the loss modulus must be separated into the contributions of the glass transition zone and the contributions of the terminal zone. In Figure 4 the loss modulus G'' of sample PB-26-0 is given in a semilogarithmic representation. The crosses are experimenal data; the dotted line corresponds to the approximate expansion of the contribution of the

Table I
Characterization of the Polybutadienes

sample	M_n (osmometry)	$M_w/M_n - 1$ (GPC)	microstructure 1,4-units (^{1}H NMR)
PB-26-0	26 000	0.05	0.94
PB-30-0	30 000	0.04	0.94
PB-35-0	35 000	0.05	0.94
PB-50-0	48 500	0.06	0.94
PB-200-0	211 000	0.1	0.94

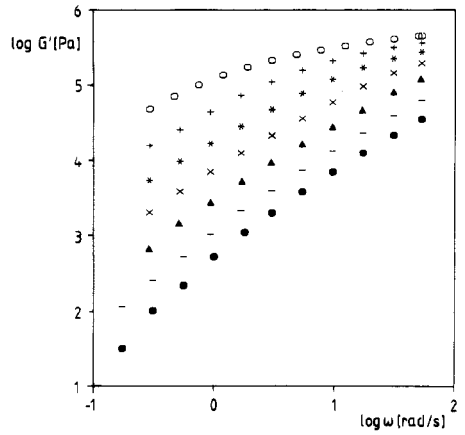


Figure 5. Reduced storage modulus isotherms for sample PB-26-5 (5% modification). Temperatures: (○) 273; (+) 283; (*) 293; (×) 303; (▲) 313; (–) 324; (●) 334 K.

terminal zone to the loss modulus. The shaded area is used to calculate G_N^0.

Experimental Section

Samples. Several samples of polybutadiene were prepared by anionic polymerization in cyclohexane at room temperature using *sec*-butyllithium as initiator. The polymerization was performed by using conventional high-vacuum techniques. The polymer was precipitated in methanol. 2,6-Di-*tert*-butyl-4-methylphenol was added as antioxidant (1 wt %). Polymers were characterized by GPC, ^{1}H NMR, and membrane osmometry. Details are listed in Table I.

4-Phenyl-1,2,4-triazoline-3,5-dione was synthesized according to the literature.[22] The modification reaction was performed in THF solution. To a 5 wt % solution of the polybutadiene in dried THF the appropriate amount of the modifying agent (dissolved in THF) was added. The reaction mixture was stirred for 2 h after the color of the 1,2,4-triazoline-3,5-dione had disappeared in order to ensure complete reaction. The sample was precipitated in methanol and dried under high vacuum. Samples were stored at 0 °C in the dark prior to use in the rheological measurements.

Viscoelastic Measurements. Rheological measurements were performed in a Instron 3250 rheogoniometer in oscillatory mode. In general, cone and plate geometry was used. Only for the highest molecular weight samples was parallel plate geometry used. Amplitudes were confined to the linear viscoelastic region. The frequencies used ranged from 0.0443 to 7.5 Hz. Measurements were performed at different temperatures. In general the temperature range covered 240–330 K. In samples with a low degree of modification even lower temperatures were used. For the samples with high degree of modification the experimental range was shifted to higher temperatures. In general the temperature span was 70–110 deg. Measurements were performed every 10 deg.

Special care was taken with regard to the temperature dependence of the measurement geometry of the rheometer system. Data were directly converted into ASCII code. All computations were performed on a HP9825 desk-top computer.

Time–Temperature Superposition. From the temperature-dependent measurements master curves were obtained. The construction of smooth master curves was possibly not only for the unmodified polybutadienes but also for the modified samples. In Figure 5 a typical set of isothermal data is shown. The modulus G' is reduced according to $G'_{red} = G'(T)T_0/T$,[13] neglecting changes of the density with temperature.

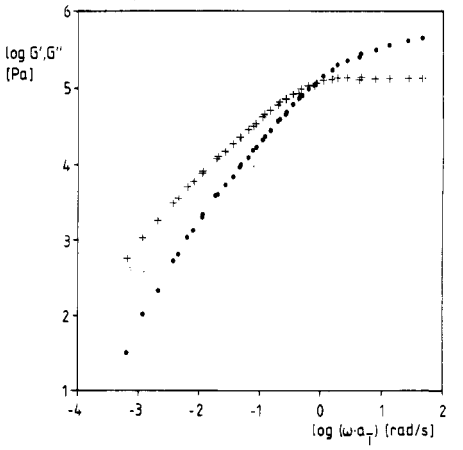


Figure 6. Master curves G' and G'' obtained by horizontal shifting of the reduced data of Figure 5 (PB-26-5).

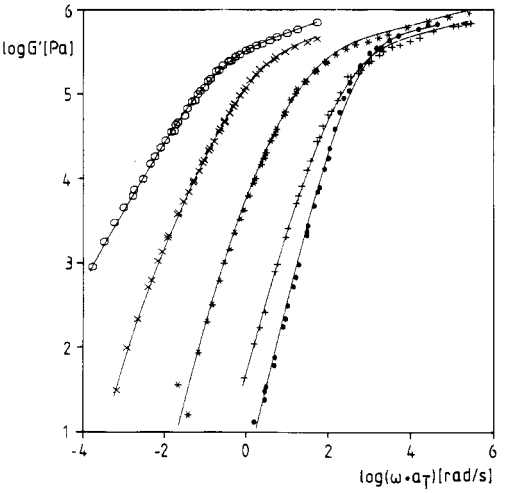


Figure 7. Storage modulus master curves for the series PB-26-x (x denotes the degree of modification in mol %): x = 0 (●), 0.5 (+), 2 (*), 5 (×), 7.5 (○). The full lines are calculated from the optimized relaxation time spectra (see text).

Despite the introduction of hydrogen bond forming groups, smooth isothermal master curves could be obtained for all samples. This is shown in Figure 6 for the data of Figure 5. The same shift factors were used for both storage and loss modulus data. This behavior implied that, despite the changes in the rheological behavior, the material behaves like a thermorheologically simple material. A more detailed discussion of the temperature dependence of the logarithmic shift factors will be given in a subsequent paper.

All master curves were reduced to 273 K as reference temperature.

Results

1. The Complex Modulus. 1.1. Influence of the Degree of Modification. In the first set of experiments the degree of modification was varied. Polybutadiene of molecular weight 26 000 (PB-26-series) was used. The degree of modification was varied between 0 and 7.5%. The latter corresponds to 36 functional groups per chain.

In Figures 7 and 8 the storage and the loss modulus master curves for this set of samples are shown. For the unmodified sample PB-26-0 the typical behavior of samples with a narrow molecular weight distribution in the flow region is observed. The slope is 2 in the log G'/log ω plot and 1 in the log G''/log ω plot. The plateau modulus G_N^0 obtained according to eq 11 is in reasonable agreement with the data obtained by Graessley.[19] With increasing modification the transition to the flow region is shifted to lower frequencies. Thus the rubbery plateau is lengthened

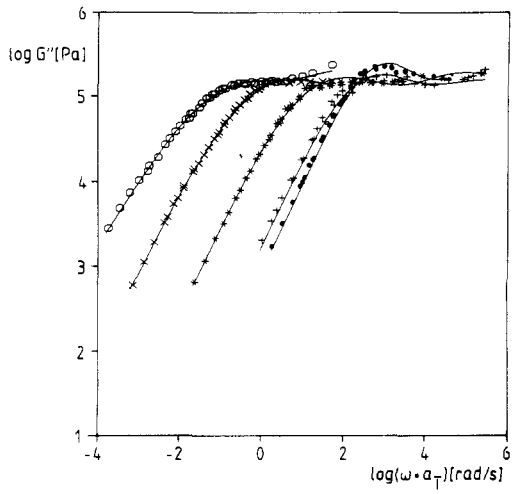


Figure 8. Loss modulus master curves for the series PB-26-*x* (symbols as in Figure 7); the full lines are calculated from the optimized relaxation time spectra (see text).

Table II
Plateau Modulus G_N^0 and M_e for the Unmodified and Modified Polybutadienes Calculated According to Equation 11

sample	$G_N^0 \times 10^{-5}$, Pa	M_e, g/mol
PB-26-0	6.0	2700
PB-26-0.5	6.0	2700
PB-26-2	6.9	2360
PB-26-5	7.1	2290
PB-26-7.5	9.1	1790
PB-35-0	7.6	2140
PB-35-1	9.1	1790
PB-50-0	7.5	2170
PB-50-1	8.6	1890
PB-200-0	8.0	2030
PB-200-1	9.2	1710

and the height is slightly increased. The values of the plateau modulus calculated according to eq 11 from the loss modulus in the terminal zone (see above) are given in Table II. With increasing degree of modification G_N^0 increases slightly. The plateau modulus of the sample PB-26-0 is slightly smaller than that for the higher molecular weight samples. From these data a molecular weight of the temporary network strands can be calculated according to

$$M_e = {}^4/_5 \rho RT/G_N^0 \qquad (12)$$

These data are also given in Table II. The results obtained for the unmodified polybutadienes are in good agreement with the values reported in the literature.[13] It is evident that the plateau modulus is mainly determined by the chain entanglements. The specific interacting sites have only a minor influence.

In addition to the low-frequency shift in the rubbery plateau, the different shape in the terminal zone is a prominent feature of the modified samples. The slope in the terminal zone decreases with increasing modification. In addition, one can notice that the slope is not constant but increases slightly with decreasing frequency. For the samples with a low degree of modification the limiting value of 2 is reached.

The loss modulus master curves show the same behavior as the storage modulus master curves. For the unmodified sample a distinct maximum in the loss modulus curve is observed. With increasing degree of modification the maximum is broadened and becomes less distinct. As for the storage modulus, the slope in the flow region is decreased.

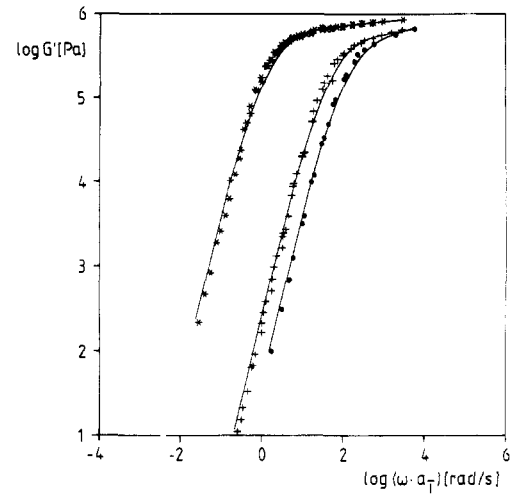


Figure 9. Storage modulus master curves for unmodified polybutadienes of different molecular weight: (●) PB-35-0; (+) PB-50-0; (*) PB-200-0. The full lines are calculated from the otpimized relaxation time spectra (see text).

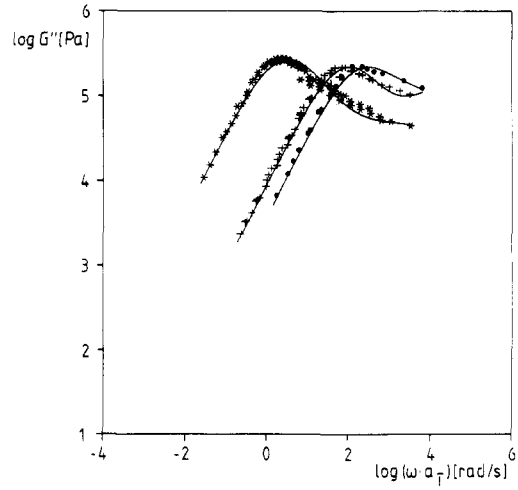


Figure 10. Loss modulus master curves for unmodified polybutadienes of different molecular weight (symbols as in Figure 9); the full lines are calculated from the optimized relaxation time spectra (see text).

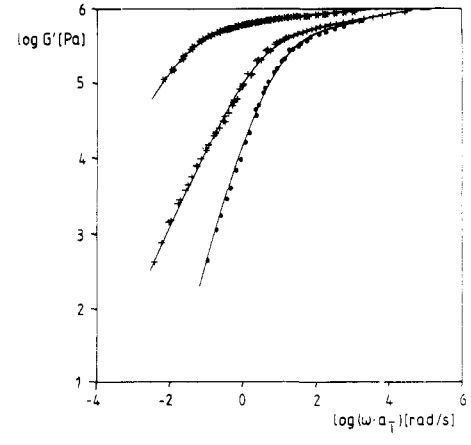


Figure 11. Storage modulus master curves for 1% modified polybutadienes of different molecular weight: (●) PB-35-1; (+) PB-50-1; (*) PB-200-1. The full lines are calculated from the optimized relaxation time spectra (see text).

1.2. Influence of the Primary Molecular Weight.

In Figures 9–12 the storage and loss modulus master curves are shown for samples with different primary molecular weight, unmodified and with 1% of the repeating units

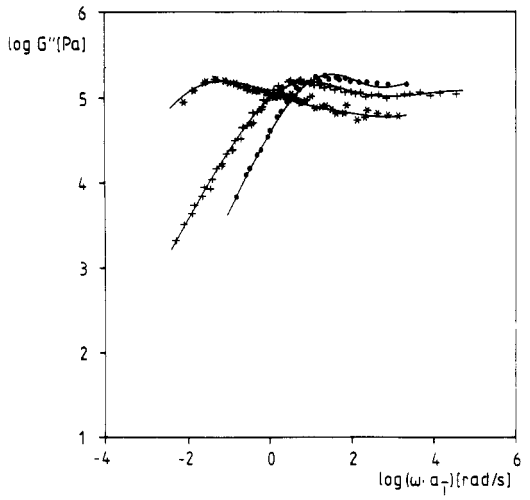


Figure 12. Loss modulus master curves for 1% modified polybutadienes of different molecular weight (symbols as in Figure 11); the full lines are calculated from the optimized relaxation time spectra (see text).

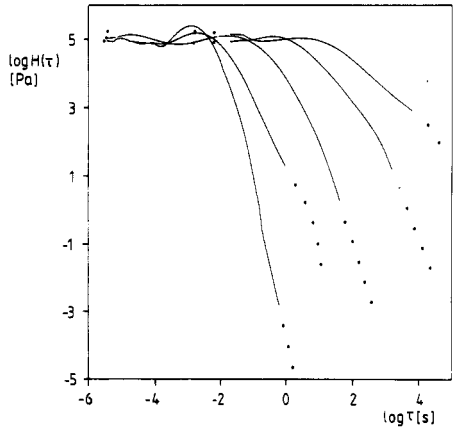


Figure 13. Relaxation time spectra of PB-26-x: the full lines correspond to the experimentally available range; the dotted lines are the expansion to shorter and longer relaxation times, required for the application of eq 6.

modified. In this case, the number of functional groups per chain is changed, while the overall concentration of functional groups is kept constant. The relative broadening in the rubbery plateau is more prominent in the case of the higher molecular weight samples. The shape of the viscoelastic functions is the same for the unmodified samples according to eq 9. The different shape of the modified samples reflects the varying number of functional groups per chain. For the modified sample with the highest molecular weight, PB-200-1, only the beginning of the flow region is observed in the experimental frequency and temperature range.

As discussed above, the plateau modulus of PB-26-0 is lower than those of the other unmodified samples. The plateau modulus of the 1% modified samples is increased by about 10–15% (Table II).

2. Relaxation Time Spectra and Equilibrium Modulus. As emphasized in the introduction, the main purpose of the present work is to obtain information concerning the properties of the network formed by hydrogen bonds. To evaluate the equilibrium mechanical properties the procedure described in the theoretical part is used. In Figure 13 the optimized relaxation time spectra are given for the PB-26 series. In all spectra a dominant maximum is observed. The maximum broadens with increasing modification. Thus the relaxation time spectra, which may be considered as a deconvolution of the loss

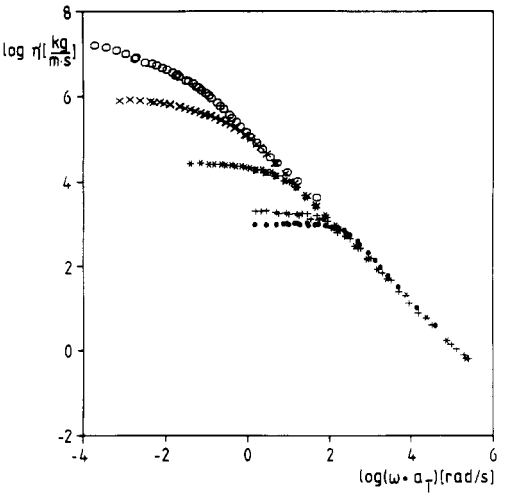


Figure 14. In-phase part of the complex viscosity as a function of frequency for PB-26-x (symbols as in Figure 7).

modulus function, reveals the same properties as the loss modulus. One advantage is the sharpening of the maximum.

From the relaxation time spectra, G' and G'' were calculated according to eq 7 and 6. The curves in Figures 7 and 8 were calculated from the relaxation time spectra. The good fit of the experimental and the calculated curves for the loss modulus shows that the computational procedure of optimizing the relaxation time spectrum works quite well. The fact that the calculated storage modulus is the same as the measured one proves that the modified polybutadienes are true viscoelastic liquids and not solids with an equilibrium modulus. The same behavior is observed for all other systems. The full lines in Figures 9–12 were calculated along the same line. In general it may be concluded on the basis of the approximate formulas derived by Tschoegl that the relaxation time spectra can be obtained equally well from G' or G''. After extension to shorter and longer relaxation times the spectra can be used to evaluate the frequency- and/or time-dependent viscoelastic functions. The observation that the calculated frequency dependence of G' coincides with the measured values proves the temporary character of the hydrogen bond junctions. This is not in contradiction to the observation that the plateau modulus G_N^0 increases slightly with the number of functional groups per chain.

3. Dynamic Viscosity. The fact that hydrogen bond junctions are not permanent even at low temperature can be readily seen from the dynamic viscosity data. In Figure 14 the master curves for the viscosity are plotted as a function of the reduced frequency. For the lower degrees of modification the Newtonian zero-shear limit is reached. With increasing degree of modification the turnover from non-Newtonian behavior to Newtonian behavior is shifted to lower frequencies. For the highest degree of modification the plateau cannot be reached but the curvature indicates that at even lower frequencies the behavior will become Newtonian. In the case of PB-200 Newtonian behavior is not reached even for the 1% modified sample. The relative increase in the zero-shear viscosity with respect to the unmodified sample can be used to describe the influence of the hydrogen bonds on the flow properties.

In Figure 15 the relative increase of the viscosity is plotted vs. the degree of modification for the samples with different molecular weight. Only those samples are included for which the Newtonian behavior was reached. The relative increase in the viscosity is different for the samples with the same degree of modification but different molecular weights. The relative viscosity enhancement

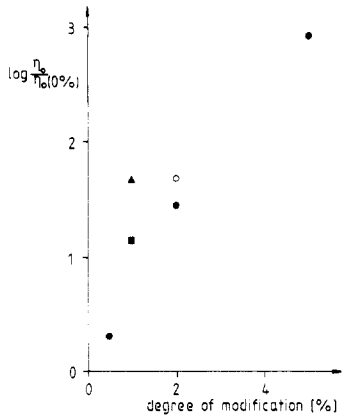


Figure 15. Relative enhancement of the zero-shear viscosity as a function of the degree of modification; different symbols correspond to different primary molecular weights: (●) PB-26-x; (○) PB-30-2; (■) PB-35-1; (▲) PB-50-1.

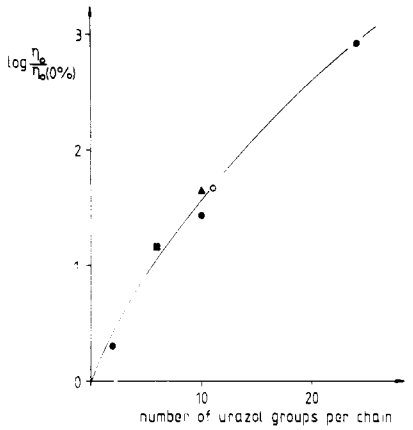


Figure 16. Relative enhancement of the zero-shear viscosity normalized for the number of functional groups per chain (symbols as in Figure 15).

increases with the primary molecular weight.

If the values of the enhancement of the zero-shear viscosity for samples with different primary molecular weights are normalized with respect to the number of groups per chain, the data fall on a single curve (Figure 16). This observation indicates that the number of hydrogen bond complexes per chain is the important quantity that determines the flow behavior. With increasing number of functional groups per chain the connectivity of the reversible network structure increases and thus the relative viscosity also increases.

4. Zero-Shear Steady-State Compliance. In melts of linear polymers the viscosity is very sensitive to the molecular weight, while the molecular weight distribution is of minor influence on the viscosity. In contrast, the recoverable steady-state shear compliance in the low shear rate limit is very sensitive to the influence of the molecular weight distribution.[23,13] The recoverable shear compliance can be used as a measure of the elastically stored energy in the limit of small deformation rates/frequencies.

For monodisperse polymers above the entanglement molecular weight, reptation theory predicts that J_e^0 is independent of molecular weight. This prediction has been verified experimentally. The values of J_e^0 for the unmodified polybutadienes in this study were also found to be independent of molecular weight and are in quite good agreement with values reported in the literature.

Introducing functional groups into the polymer backbone causes the recoverable compliance to increase strongly. This is shown in Figure 17 for the PB-26 series. For the highest degrees of modification the limiting value

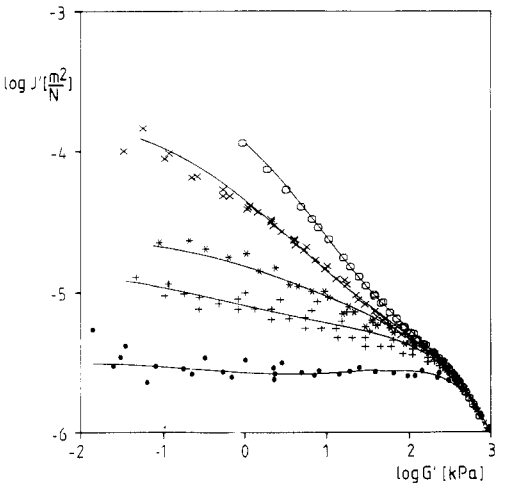


Figure 17. Compliance calculated according to eq 3 plotted vs. the storage modulus[23] for PB-26-x (symbols as in Figure 7).

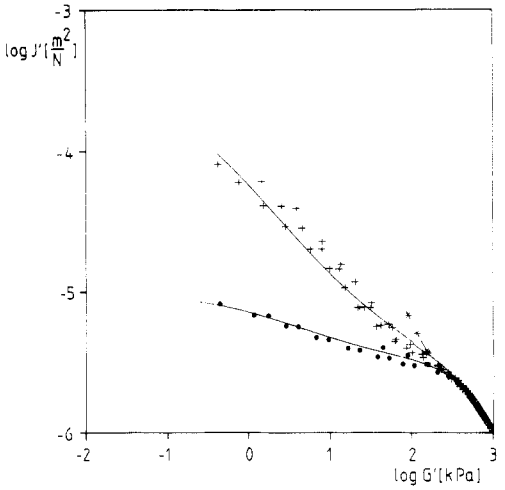


Figure 18. Compliance calculated according to eq 3 plotted vs. the storage modulus for different primary molecular weight and 1% modification (symbols as in Figure 11).

is not reached. In Figure 18 the data for the compliance vs. log G' are plotted for different primary molecular weights in the case of 1% modification. It is evident that the compliance behavior strongly depends on the primary molecular weight. Again the behavior of the compliance may be interpreted qualitatively in terms of the increased connectivity with increasing modification and increasing primary molecular weight.

Discussion

The results described in the previous sections give a convincing picture of the viscoelastic properties of a polymer chain carrying strongly interacting functional groups statistically distributed along its chain contour. The modulus as well as the viscosity behavior are consistent with the picture of a reversible association of a multifunctional polymer. This association induces an apparent increase in the viscoelastic effective molecular weight. Through the association large, reversible, branched clusters are formed. The cluster structure varies with time and temperature. Such branched clusters are responsible for the increase in the steady-state shear compliance J_e^0, which may be interpreted in a simplified way, according to the behavior of linear chains, as being due to a strong increase of the effective polydispersity.

The result of the analysis from the relaxation time spectra, showing that these thermoreversible networks do not have an equilibrium network modulus, is consistent

with the observation of a Newtonian flow at very low frequencies. It would be interesting to perform a similar analysis on sulfonated EPDM's with ionic interacting groups. On the other hand, for SBS-type thermoplastic elastomers an equilibrium modulus has been calculated by using a similar type of analysis. This substantiates the conclusion that thermoreversible network structures formed by randomly distributed functional groups are of a different nature than phase-separated systems.

The general effect on interacting groups is a shift of the terminal relaxation times to long times by imposing additional restrictions on the relaxing chains. By the same restrictions, the plateau modulus is increased. In many applications, where deformation is only applied for short times, or good damping properties are required over an expanded time scale, such thermoreversible associations may be sufficient.

The present study clearly reveals the relation between molecular parameters, such as primary molecular weight and degree of modification, and viscoelastic properties of polymer melts with strongly interacting functional groups. Nevertheless several problems remain to be solved for these systems. A quantitative analysis requires the knowledge of the fraction of hydrogen bonds formed. A preliminary study shows that the fraction of free and bound units may be derived from IR spectroscopy.[11] These studies are presently extended to a wider range of temperatures and for different degrees of modification. In this context it is important to determine whether the thermodynamic equilibrium concentration of hydrogen bonds of analogous low molecular weight model compounds is reached in polymer melts, or whether topological restrictions imposed on the interacting groups, because they are fixed to a polymer backbone, become important.

To study the structure of the thermoreversible aggregates different methods must be applied. The structures formed by thermoreversible association will be accessible from light-scattering measurements in the dilute and semidilute regime.

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Kinetic Observations by SAXS and Centrifugation of a Gelating System

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ABSTRACT: We report observations from two distinct experiments of a system gelating in the presence of external constraints, an intense X-ray beam from a synchrotron source and the acceleration field of a centrifuge. In both these experiments on poly(acrylamide/bisacrylamide), a substantial fraction of the sample remains in the sol phase in coexistence with the developing gel. Kinetic observations by small-angle X-ray scattering (SAXS) and the Schlieren optics of the analytical centrifuge reveal that gelation is not necessarily the monotonic process that is found in samples gelling under uniform conditions, but can take the novel form of a series of separate gelation avalanches, each generation interpenetrating with the established structure of the previous gelation. These oscillations, fueled by monomers from the sol phase, are a consequence of the nonlinearities of the gelation process coupled with the delay due to diffusion of the monomers through the existing gel structure. The changes in the scattering function seen by SAXS permit comparisons with observations made by other authors on gelling systems.

Introduction

Gelating systems have recently been the object of much theoretical and experimental scrutiny, particularly with regard to which model best describes the sol–gel transition.[1] Close to this point, measurements of shear modulus,[2] viscoelasticity,[3] and permeability,[4] as well as light[5,6] and neutron[7] scattering measurements on interrupted polymerization reactions, have found broad agreement with the percolation model of gelation, the validity of which now seems generally accepted.

An important precaution taken in observations of ge-

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