is prepared by adding the γ-APS to the melt containing PA6 and glass microspheres, some poly(γ-APS) is formed in the polymer matrix itself. In the spectrum of the polymer fraction of D, no ^{29}Si is visible, indicating that the layer of siloxane from pretreatment remains firmly attached to the glass microspheres.

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Registry No. PA6, 25038-54-4; γ-APS, 919-30-2.

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Relaxation Behavior of Linear Polymer Chains with Statistically Distributed Functional Groups

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ABSTRACT: On the basis of the Doi–Edwards model of reptation, the terminal relaxation properties of a linear polymer melt in which the monodisperse polymer chains carry a certain number N of associating functional groups is described. The relaxation behavior is strongly influenced (i) by the mean lifetime of the complexes formed between two functional groups and (ii) by the mole fraction of complexed groups. Tube renewal processes are incorporated into the model. The theoretical relaxation curves are in qualitative agreement with corresponding experimental results obtained for a model system.

Introduction

The linear viscoelastic properties of polymer melts are strongly influenced by the presence of a few functional groups. Typical examples are ionomers like sulfonated EPDM rubbers or polystyrene sulfonates.[1,2] Considerable experimental work dealt with the influence of parameters like the polarity of the surrounding medium and counterion and degree of modification on the bulk and solution properties.[3,4] Recent work on ionomeric model systems (halatotelechelics) showed that the association behavior is governed by well-defined ionic clusters with 10–12 ionic dipoles associated to a multiplet.[5,6] To describe theoretically the behavior of polymers with associating groups, it is generally assumed that dimeric complexes between the ionic groups are formed.[7-9] The main focus of these investigations was the behavior in dilute solution; especially the coil collapse due to the interacting groups has been considered.[9] No theoretical description of the dynamic behavior of ionomers, which accounts for the detailed picture of the different levels of molecular organization, is available.

To elucidate the basic assumptions of the theoretical models, appropriate model systems must be chosen. We have reported on the formation and the rheological properties of thermoreversible networks, where the junctions are formed by a defined hydrogen-bond complex between two functional groups.[10,11] In such a system, IR spectroscopy of the hydrogen-bond complex[12] allows a direct relation between complex formation and the mechanical properties. It should be mentioned that Longworth and Morawetz[13] reported on the influence of hydrogen bonding on the melt viscosity in styrene–methacrylic acid copolymers as early as 1958. The experimental techniques now available allow a more detailed analysis. In addition, the interpretation of rheological data should be simplified by the use of polymers of narrow molecular weight distribution.

In this paper, a simple theoretical model that describes the flow behavior of polymers with a defined number of functional groups is presented based on an approach first introduced by González.[8] The model is based on the concept of relaxation by reptation,[14] and the effect of associating groups is introduced into the tube model of Doi and Edwards,[15] including extensions that take into account the tube renewal processes.[16-18]

Theoretical Model

The polymer melt consists of linear monodisperse polymer chains with degree of polymerization P_n. A small fraction u (=degree of modification <5%) of the repeating units carries the functional groups U, which are able to form dimeric complexes. Thus, the number of functional groups per chain N is given by $P_n u$. Complexation is described by the equilibrium reaction

$$\mathrm{U} + \mathrm{U} \xrightarrow{K_0} \mathrm{U}_2 \qquad (1)$$

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The mole fraction of complexed units x_2 is given by

$$x_2 = a/2 - ((a/2)^2 - 1)^{1/2} \qquad (2)$$

$$a = 2 + 1/(2K_0[\mathrm{U}_0])$$

where K_0 is the equilibrium constant and $[\mathrm{U}_0]$ is the molar concentration of functional groups.

In contrast to cooperative phenomena observed in the association behavior of many biopolymer systems,[19,20] it is assumed that complex formation occurs independently for each functional group. As has been discussed previously, an "anticooperative" phenomenon, due to topological constraints, may play an important role, when complex formation in statistically substituted polymers is considered.[21]

The rheological properties of high molecular weight polymer melts can be described according to the concept of reptational motion. On the basis of reptation of the polymer chain in a constraining matrix, both, the Curtiss–Bird model[22] and the Doi–Edwards model,[15,16] were developed.

In the Doi–Edwards model, the chain is located inside a tube of constraints, formed by the surrounding polymer chains. The polymer chain performs a curvilinear diffusion along the main chain direction but cannot move perpendicular to this direction. The stress relaxation modulus $G(t)$ is obtained in the Doi–Edwards model according to

$$G(t) = G_N{}^0 \sum_{p=\mathrm{odd}} 1/p^2 \exp(-tp^2/\tau_\mathrm{d}) \qquad (3)$$

τ_d is the characteristic relaxation time for the reptation process. The sum is dominated by the first component where $p = 1$. Thus, the relaxation behavior can be described roughly by a single-exponential decay.[23] The upper limit is given by the number of Rouse subchains according to

$$p_\mathrm{max} = M_\mathrm{w}/M_\mathrm{e} \qquad (4)$$

where M_w is the molecular weight of the polymer and M_e is the molecular weight between topological entanglements.

Equation 3 is only a first approximation, and additional motions, which contribute to stress relaxation, have been added to account for the more complex real behavior. The most important are tube renewal (constraint release)[17,18] and tube length fluctuation mechanisms.[16,24] While the first accounts for the influence of the relaxation of the surrounding matrix on the relaxation behavior of the polymer chain under consideration, tube length fluctuations contribute to the stress relaxation on the high-frequency (short-time) end of the terminal relaxation behavior.

Tube renewal processes have been introduced by several authors in different ways.[16-18] The main assumption is that the probability for the removal of a part of the tube depends on the relaxation rate of the surrounding chains. Consequently, in the case of a melt of chains of uniform length, tube renewal follows the same time dependence as reptation itself. Since the relaxation in the terminal zone is primarily governed by the contribution of the exponential with $p = 1$, the equation for the stress relaxation including tube renewal can be written as

$$G(t) = G_N{}^0 \exp(-t/\tau_\mathrm{d}) \sum_{p=\mathrm{odd}} 1/p^2 \exp(-tp^2/\tau_\mathrm{d}) \qquad (5)$$

When any special model is neglected, the terminal relaxation behavior is described by the longest relaxation time. In the Doi–Edwards model, this longest relaxation time corresponds to the time, t, after which the chain has left the tube where it was constrained at time 0.

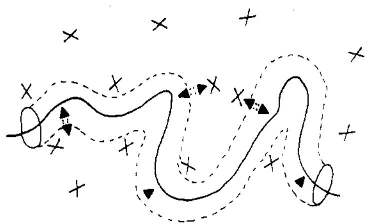

Figure 1. Section of a linear polymer chain with functional groups (▲), with the complexed fraction x_2u (◄::►) within a tube defined by the surrounding chains (×).

In the following, the effect of associating functional groups (stickers) has to be taken into account. This will be done according to the scheme developed by González for ionomer solutions.[8] A segment of a chain with uP_n stickers is shown in Figure 1. The fraction, x_2, of these stickers forms dimeric complexes. Thus, the chain is not only confined by the tube (entanglement network) as usual in polymer melts but also by the thermoreversible junctions, U_2. The chain under consideration has N functional groups, $N_2 = x_2N$ of which are complexed. It is assumed for the moment that every chain carries the same number of stickers. It is evident that any type of relaxation mechanism involving segments with complexed units will be strongly hindered as long as the functional group is part of a complex. While local conformational rearrangements in the chain will only be influenced by the directly neighbored complexes, long-range rearrangements, like reptational motion of the whole molecule, are influenced by many of the complexes. González assumed that pure reptation can only occur when a chain is not complexed; i.e., no sticker of the chain takes part in a complex. Though very restrictive, this assumption will be used to model the terminal relaxation behavior.

It is known that, for free chains incorporated in covalently cross-linked networks, reptation is the dominating relaxation process. Tube renewal mechanisms are strongly reduced in those systems. If the rearrangement of the network structure is slow compared to the motion of a single chain, reptation should be the dominating relaxation path. On the other hand, if the reptation of the chains is strongly reduced by complexation, tube renewal, as well as tube length fluctuations or fluctuations of dangling ends as introduced by Graessley,[16] may become important. In the first attempt to describe the characteristic features of the system, only reptation and reptation including tube renewal, according to eq 5, will be considered.

If $\tau_\mathrm{d}{}^0$ is the reptation time of the chain without stickers (functional groups), τ_d is the corresponding reptation time of the chain with N stickers, and reptation can only occur for the fraction of time, f_t, in which the chain is not complexed, one can write

$$\tau_\mathrm{d} = \tau_\mathrm{d}{}^0/f_t \qquad (6)$$

Thus, f_t describes the probability that the chain is free and can reptate as a whole. Of course, this assumption will fail if relaxations including only parts of the polymer chain contribute significantly to the overall relaxation in the terminal zone.

If N_2 groups are complexed, each of these complexed groups contributes to the hindrance of the reptational motion. In the most simple case, where any group makes the same contribution, f_t is given by

$$f_t = f_{t1}{}^{N_2} \qquad (7)$$

where f_{t1} is the fraction of time that a unit U is not complexed and allows the chain to reptate. In principle, the lifetime of the complex is given by the rates of decomplexation and complexation. For low molecular weight hydrogen-bond complexes, the rate constant or frequency of decomplexation of systems analogous to those considered in the present context is on the order of 2×10^7 M^{-1} s^{-1},[25] which is much higher than the frequency of the mechanical measurements. Thus, the rate of decomplexation is not the important quantity which determines the rheological behavior. Moreover, we are interested in the fraction of time, f_{t1}, in which the group is not complexed. Thus, f_{t1} is the probability that the group is not complexed. This probability can be expressed simply by the mole fraction of uncomplexed units, x_1:

$$f_{t1} = x_1 = 1 - x_2 \tag{8}$$

This equation is valid if the interesting time scale of relaxation is long compared to the complexation kinetics. The reptation time, τ_d, of a chain with N_2 complexed functional groups is given by

$$\tau_d = (1 - x_2)^{-N_2}\tau_d{}^0 \tag{9}$$

If this result is used to calculate the relaxation modulus, $G(t)$, according to eq 3 and 5, the resulting relaxation curve has the same general behavior. The only difference is that the relaxation function is shifted to longer times, i.e., lower frequencies for a dynamic experiment. This is a consequence of the simplified picture that all chains have the same number of functional groups. If a distribution of the number of functional groups per chain is considered, as is the case in a real system, the relaxation properties will change. For pure reptation, the stress relaxation modulus is given in this case by

$$G(t) = G_N{}^0 \sum_{n=1}^{\infty} W(P_n;n,u) \sum_{p=\mathrm{odd}} 1/p^2 \exp(-tp^2/\tau_{dn}) \tag{10}$$

where $W(P_n;n,u)$ is the probability that a chain with degree of polymerization, P_n, carries n functional groups if the degree of modification is u. For $u \ll 1$, the Bernoullian distribution, $W(P_n;n,u)$, simplifies to the Poisson distribution; i.e.,

$$W(n) = N^n/n! \exp(-N) \tag{11}$$

where N is the average number of functional groups per chain, $N = uP_n$, as defined above. For any chain with a different number of functional groups, n, a different reptation time, τ_{dn}, must be used.

This effect is similar to that of a distribution of relaxation times due to polydispersity. Of course, the molecular origin is quite different. It has been discussed in detail by Rubinstein et al.[17] that the effect of a broad distribution of relaxation times especially influences tube renewal processes. Especially those "tube-forming" chains with short relaxation times will contribute to the renewal of the chain which is considered. In accordance to the notation given in eq 5 and 10, the stress relaxation modulus, including tube renewal and the distribution of relaxation times, is given by

$$G(t) = G_N{}^0 \sum_{n=1}^{\infty} W(P_n;n,u) \exp(-t/\tau_{dn}) \sum_{n=1}^{\infty} W(P_n;n,u) \times \sum_{p=\mathrm{odd}} 1/p^2 \exp(-tp^2/\tau_{dn}) \tag{12}$$

In Figure 2 the stress relaxation modulus, $G(t)/G_N{}^0$, is plotted versus the reduced time $t/\tau_d{}^0$ for the Doi–Edwards model (eq 3), the Doi–Edwards model including tube renewal (eq 5), and the corresponding curves for a chain with an average number of $N = 10$ functional groups and an equilibrium constant $K_0 = 5$ ($x_2 = 0.58$) (eq 8 and 12). As expected, the terminal zone shifts to longer relaxation times. If tube renewal is taken into account, the shift is less pronounced, which seems to be more realistic. Equation 12 will be used to discuss the influence of the concentration and of the complex stability on the viscoelastic behavior.

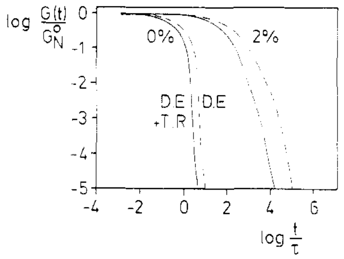

Figure 2. Calculated stress relaxation modulus $G(t)/G_N{}^0$ versus the reduced time $t/\tau_d{}^0$ for the Doi–Edwards theory (eq 3), Doi–Edwards theory including tube renewal (eq 5), and modified Doi–Edwards theory without (eq 8) and with tube renewal (eq 12) (chain with 10 functional groups ($P_n = 500$, $K_0 = 5$, $u = 2\%$)).

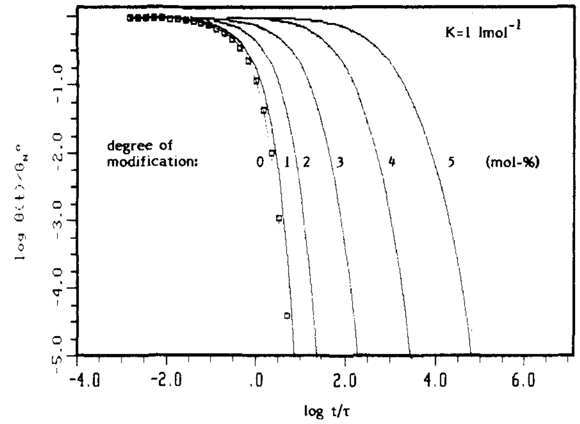

Figure 3. Influence of the degree of modification (u) on the relaxation modulus $G(t)$ (eq 12); $P_n = 500$, $K_0 = 1$.

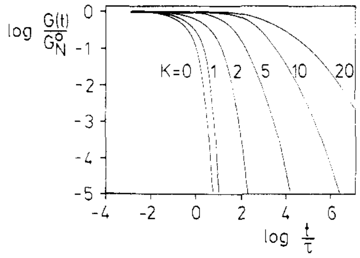

Figure 4. Influence of the equilibrium constant (K_0) on the relaxation modulus $G(t)$ (eq 12); $P_n = 500$, $u = 2\%$.

In Figure 3 the influence of an increasing concentration of functional groups is shown. The equilibrium constant, K_0, is kept constant. Of course, as a consequence of eq 2, the mole fraction of complexed units increases with increasing overall concentration. With increasing concentration the relaxation curves are shifted to longer times with little change in the curvature. In Figure 4 the concentration of functional groups is kept constant ($u_0 = 0.02$) and the equilibrium constant is varied from 1 to 20. This variation in the equilibrium constant at constant concentration of functional groups corresponds to an increase in x_2. Thus, according to the previous discussion, it is equivalent to an increase in the average lifetime of a complex. The relaxation curves are not only shifted to higher values of $t/\tau_d{}^0$, but also the transition from the rubbery plateau to flow occurs more gradually. This broadening in the transition from the rubbery plateau to the terminal zone is also observed experimentally.[10,11] A quantitative check of the limits of the model affords an independent determination of the mole fraction of com-

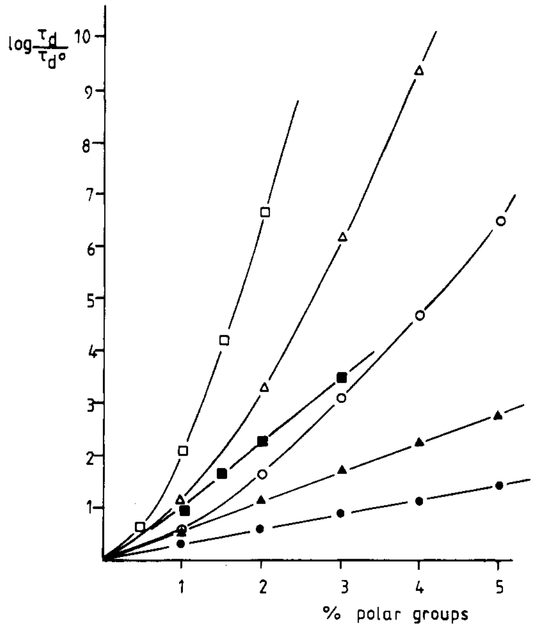

Figure 5. Increase in the terminal relaxation time, log (τ_d/τ_d^0), as a function of the degree of modification for different chain length without (open symbols) and with (closed symbols) topological restrictions (see text); P_n = 250 (○), 500 (△), 1000 (□); K_0 = 10.

plexed groups x_2, i.e., by a spectroscopic technique.[12] In the following sections of this paper, the terminal relaxation behavior and the influence of topological constraints on the association and relaxation behavior will be discussed.

The Terminal Relaxation Behavior

A semiquantitative test of the theoretical predictions can be obtained from the analysis of the terminal relaxation behavior. From eq 8, the increase of the terminal relaxation time τ_d/τ_d^0 is given by

$$\tau_d/\tau_d^0 = (1 - x_2)^{-N_2} \tag{13}$$

or in logarithmic terms

$$\log (\tau_d/\tau_d^0) = -N_2 \log (1 - x_2) \tag{14}$$

The limiting behavior (no groups complexed) is given correctly by this equation, if it is assumed that the monomeric friction coefficient, ξ_{00}, of the chain segments carrying functional groups is not altered. For $x_2 = 0$, $\tau_d = \tau_d^0$. The opposite extreme, $x_2 = 1$, is achieved for infinitely large equilibrium constant, K_0, i.e., for a covalently cross-linked system. If there is only one group attached to the surrounding matrix, the terminal disengagement time is infinite. Here the limitations of the model are evident. No relaxation according to fluctuating chain ends has been taken into consideration.

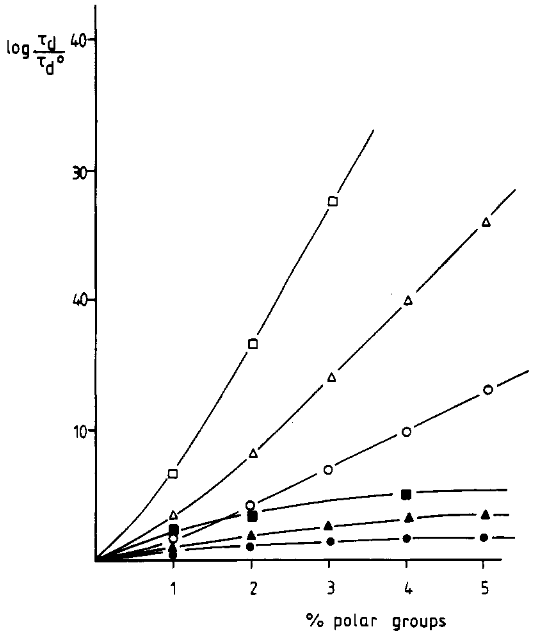

Figure 6. Increase in the terminal relaxation time, log (τ_d/τ_d^0), as a function of the degree of modification for different chain length without (open symbols) and with (closed symbols) topological restrictions (see text); P_n = 250 (○), 500 (△), 1000 (□); K_0 = 100.

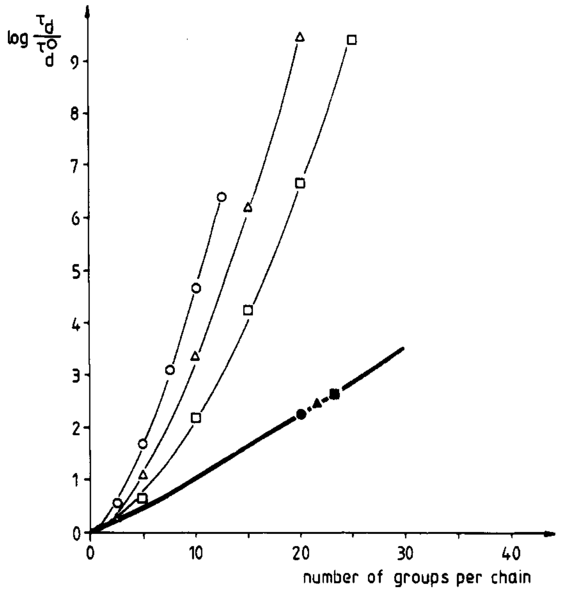

Figure 7. Increase in the terminal relaxation time, log (τ_d/τ_d^0), as a function of the number of functional groups per chain for different chain length without (open symbols) and with (closed symbols) topological restrictions (see text); P_n = 250 (○), 500 (△), 1000 (□); K_0 = 10.

The increase of the longest relaxation time, log (τ_d/τ_d^0), depends on the number of functional groups per chain and the mole fraction of complexed units. The latter quantity varies with K_0, i.e., the temperature and the concentration of functional groups, which can be varied either by the degree of modification or by the concentration of polymer in the system. The variety of parameters, which influence log (τ_d/τ_d^0), is illustrated in Figures 5–8 (open symbols). In Figures 5 and 6, log (τ_d/τ_d^0) is plotted versus the degree of modification for chains of various length for K_0 = 10 and 100. At constant degree of modification, τ_d/τ_d^0, is larger for high molecular weights, because the number of groups per chain is larger. If the same data are plotted versus the number of groups per chain (Figures 7 and 8), the shortest chain length shows the most pronounced upturn, because the concentration of units is larger for the same number of functional groups per chain. According to Le Chateliers principle, the increasing concentration of units will increase x_2.

The Effects of Topological Constraints

In the previous section, the mole fraction of complexed units is calculated according to eq 2 with the equilibrium constant, K_0. According to the laws of thermodynamics, the equilibrium constant, K_0, is independent of the concentration. If the situation is treated in more detail, the activities must be considered rather than the concentration. If functional groups are attached to a polymer backbone, additional complications may arise due to the fact that a functional group is restricted to a certain volume

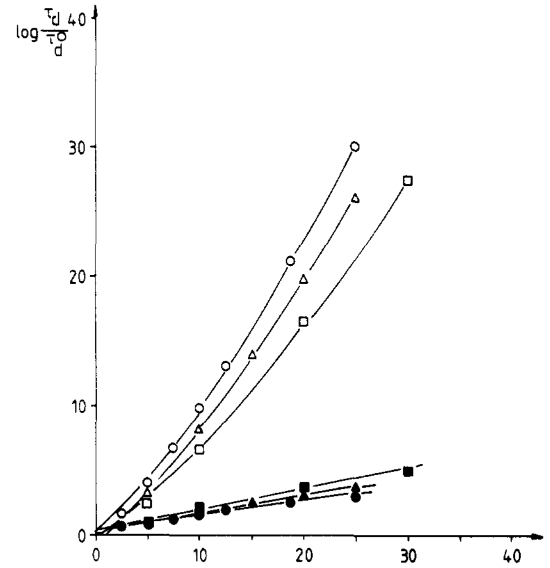

Figure 8. Increase in the terminal relaxation time, log (τ_d/τ_d^0), as a function of the number of functional groups per chain for different chain length without (open symbols) and with (closed symbols) topological restrictions (see text); P_n = 250, (○), 500 (△), 1000 (□); K_0 = 100.

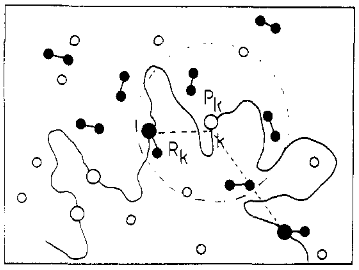

Figure 9. Topological constraint on a functional group (k) restricted to the volume (V_k) by the neighbored complexed groups (small symbols: functional groups of other chains); (○) complexed functional groups; (●) free functional groups.

by the constraints arising from topologically neighbored complexes ("topological constraint"). This is shown schematically in Figure 9. The uncomplexed group k located at P_k is restricted to a certain volume V_k to find another free group for complexation. The size of V_k is given by the distance R_k to the topologically next neighbored complexed group. The evaluation of the effect of the chain topology on the association behavior has been treated in detail in a previous paper.[21] As a final result, the fraction of effectively complexed units, x_2^{eff}, is given by

$$x_2^{\mathrm{eff}} = \sum_{n=1}^{\infty} W(n) x_2^0/n\left[1 + \sum_{k=2}^{n} \int_0^{R_k} w(r)\right] \qquad (15)$$

with

$$w(r) = (\beta/\pi^{1/2})^3 \exp(-\beta^2 r^2)\, 4\pi r^2\, \mathrm{d}r$$
$$\beta = 1/d_u$$

where d_u is the distance between free functional groups and R_k depends on the number of complexed groups in the chain and on the chain flexibility given by the characteristic ratio, C^∞. For shorter polymer chains, the effect of the polydispersity of functional groups must be taken into account for the calculation of x_2^{eff}. The influence of the effect of the connectedness of the functional groups on the association behavior was shown experimentally by IR spectroscopy. For a low molecular weight model compound, the mole fraction of complexed groups was found to be considerably larger than for the polymeric system.[26] If the topological constraints are taken into account, the results concerning the increase of the terminal relaxation time change. This is shown by the closed symbols in Figures 5–8. For these calculations, the characteristic ratio, C^∞, was taken as 1.0 (l_0 = 0.5 nm, n is the number of monomers). In Figure 10, the effect of chain flexibility is shown. The functional group k, attached to the polymeric chain, has to find a free functional group within a volume V_k (see Figure 9) which decreases with decreasing C^∞ (increasing chain flexibility). Thus, the effect of the topological constraints is enhanced. It has been mentioned in the previous paper that contributions of the chain topology to the local order are not considered in this treatment. According to Figures 5 and 6, the differences calculated for different primary molecular weight chains in the absence of topological restrictions vanish, if such constraints are taken into consideration.

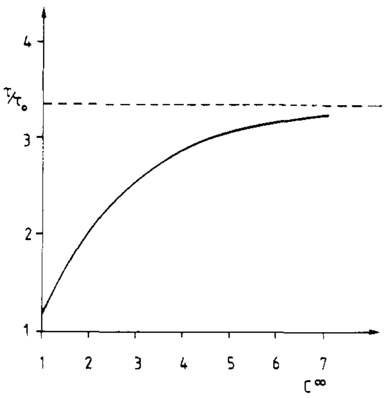

Figure 10. Influence of the chain flexibility, expressed in terms of C^∞ on the terminal relaxation time modified by topological restrictions; K_0 = 10, P_n = 500, u = 2%.

Comparison with Experimental Data

The increase in the terminal relaxation time can be obtained for the experimentally available data from the zero shear viscosity and the recoverable steady-state shear compliance $\tau_d = \eta_0 J_e^0$, provided that reptation is the dominating relaxation mechanism for long-range conformational rearrangements and that simple reptation is hindered by the presence of the associating functional groups. In previous work, we have reported on the linear viscoelastic properties of polybutadienes with narrow molecular weight distribution, which are modified by introducing polar urazole groups, which form hydrogen-bond complexes.[11] For systems with a low number of functional groups per chain (low degree of modification or low molecular weight), the limiting values of η_0 and J_e^0 can be determined. In Figure 11 the experimentally observed increase in the terminal relaxation time, log τ/τ_0, is plotted as a function of the number of functional groups per chain. The thin solid line was calculated according to eq 14, neglecting the influence of topological constraints, while the thick one was calculated, including the effect of topological constraints. For this calculation, the characteristic ratio was taken to be $C^{\infty\prime}$ = 4.2 as reported for polybutadiene[27,28] and the equilibrium constant, K_0, was 330 L/mol, a value which has been obtained from IR spectroscopy studies on a low molecular weight model.[26] In order to show the different behavior with and without topological constraints, the values for K_0 = 2 and 75 without topological restrictions are shown (- - -). It can be seen that the simple model presented here gives qualitatively the right prediction, if the topological influence is taken into account. The fact that the data for different

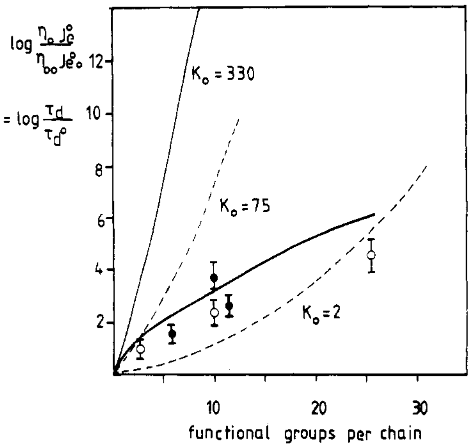

Figure 11. Increase of the terminal relaxation time, log (τ_d/τ_d^0) = log $(\eta_0 J_e^0/\eta_{00} J_{e0}^0)$, as a function of the number of functional groups; the experimental data were obtained for polybutadiene with narrow MWD;[10,11] (○) $M_n = 26\,000$, various degrees of modification; (●) various molecular weights at 1% modification; the values were obtained from reduced data at 273 K. The corresponding equilibrium constant for a low molecular weight model[26a] is 330 L/mol; (—) theoretical curve without topological restrictions; (–) theoretical curve including topological restrictions ($P_n = 500$, $C^{\infty\prime} = 4.2$). The other curves were obtained using the equilibrium constants as indicated.

primary molecular weight chains are given by the same curve might support the basic model including the effect of the influence of the topological constraints on the complex formation. Nevertheless, it is not possible at present to describe the relaxation function as a whole. The model also fails, if samples with a large number of functional groups are considered.

As has been mentioned above, the major fault in the present model arises from the assumption that chain reptation can only occur when all functional groups are dissociated. A more realistic treatment will have to account for the relaxation of subchains which actually occurs, as can be seen from the broadening of the relaxation time spectrum in Figure 3 of ref 11. In the present form, the model mainly accounts for a shift in the relaxation time spectrum to longer times. This deficiency also becomes clear, if not only the terminal relaxation time is considered but the changes of both viscosity (η_0) and recoverable compliance (J_e^0) are considered separately. It turns out that the increase in η_0 is predicted to be too large, while the increase of J_e^0 is predicted smaller than observed experimentally.[29] This is a consequence of the fact that relaxation processes of parts of the chains are not incorporated properly in the model.

The more basic question is whether reptation actually is the correct relaxation process for a polymer melt with strong associations between the chains. Recent experiments have shown that this will only be the case if the number of groups per chain is small.[30] In the limit of a small number of functional groups per chain, the treatment given in this paper appears to work reasonable well.

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