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Association behavior of binary polymer mixtures under elongational flow

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The influence of elongational flow on the association behavior of binary mixtures of functionalized polymers capable of forming single reversible orientationally dependent bonds, such as hydrogen bonds, is studied analytically. Applying a mean-field approach with an external potential representing the effect of the elongational flow, the orientation distribution functions for the dumbbell model and the freely jointed model of a polymer chain were obtained. Two opposite factors determine the association of ''linear'' diblock copolymerlike chains: the unfavorable extra stretching under flow of associated polymer chains and the favorable orientation of the chains (segments) along the flow direction. The former dominates and the fraction of associated ''linear'' chains decreases with increasing flow rate. For mixtures of polymers which are capable of forming associated T-chains, the association also decreases, however, more slowly, and this time due to unfavorable orientational effects. If the formation of associated linear and T-polymers as well as complex linear/T-polymers is possible, a strong preference for the formation of associated T-chains is found. At high flow rates any type of association becomes unfavorable. © *2000 American Institute of Physics.* [S0021-9606(00)50135-4]

I. INTRODUCTION

Polymer blends consisting of associated one-end functionalized polymers have become the subject of several experimental and theoretical investigations recently.[1–6] The phase behavior of mixtures of two homopolymers carrying a functional group at one end and capable of forming associated diblock copolymer-like chains combines features of both homopolymer blends and block copolymer melts.[1–8] In what follows we will consider reversible orientationally dependent association such as hydrogen bonding,[9,10] where a bond between donor and acceptor groups can arise only when they are at the correct orientation with respect to each other (Fig. 1).[9] This implies a loss of orientational entropy, as will be discussed below. Since the relative energetic gain for association varies with temperature, the total contribution of both energetic and entropic factors leads to a strong temperature dependence of the degree of association.[11,12] As a result, hydrogen bonded polymer systems exhibit characteristic phenomena, such as the reappearance of the stable homogeneous phase for decreasing temperatures.[7,8,10–15] The association and hence the phase behavior of such polymer blends may become even more intriguing if some external field (such as a flow field) capable of changing the association rate is applied. The effect of an external elongational (flow) field on the association behavior of a mixture of one-end functionalyzed associating polymers is the subject of the present analytical investigation. The discussion will be limited to functional groups that can participate in a single association only (cf. Fig. 1).

Reversible association of many polymers (surfactants) into long ''linear'' chains[16–18] or networks[19] in the absence of flow has been studied in detail. Some rheological properties of these polymer systems have also been addressed,[20–24] however the investigations concern mainly general macroscopic properties, rather than the association behavior of individual chains. The influence of flow fields on phase behavior of ordinary polymer solutions and polymer blends has been studied in detail both theoretically and experimentally.[25–33] A complex interplay has been found between the thermodynamic incompatibility of the components and the compatibilizing/separating tendency driven by the difference in elastic (hydrodynamic) properties of the chains. The combined effect of these two does not seem to have a universal character (at least at small or intermediate flow rates) and may lead to both mixing and demixing effects depending on the particular polymer system, type of flow, and angle of observation.

The effect of flow on block copolymer melts (solution) has also a complex character.[34–41] By varying the flow rate it is possible to manipulate the orientation as well as to force phase transitions between different ordered structures. Flow may also promote or hinder separating tendencies depending on the system composition, chain (block) lengths, and so on. Rheological properties of hydrogen bonded[21–24,42] and other types of associated polymer systems[20,43–47] attracted much attention recently. Because of the complexity of the behavior of associated polymer systems even in the absence of flow, the analysis of the rheological properties is an interesting, but formidable task.

In the present article we will limit ourselves by considering only the influence of an external elongational (flow) field on the association behavior under steady state conditions. We will analyze the behavior of binary blends of relatively short chains, so that any entanglement effects may be

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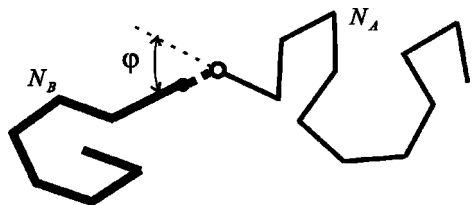
FIG. 1. Schematic picture of associated (hydrogen bonded) ''linear'' polymers.

ignored. To analyze the association behavior we will apply a mean field approach in which the influence of the flow will be accounted for by the corresponding external potential acting on the chains (the hydrodynamic resistance of segments is supposed to be the same for both chains). We will consider relatively small flow rates assuming that there is a quasiequilibrium in the polymer system at some chosen flow rate, so that no hysteresis or ''prehistory'' effects will be taken into account.

To analyze the influence of flow on the association rate, it is necessary to take into account two important effects: chain elongation and chain orientation. Elongation and overall orientation of polymer chains under flow has been studied in detail experimentally,[48–53] theoretically,[54–58] and by computer simulations.[59–61] Some of the theoretical approaches developed will be applied in the present article for estimating the entropy loss accompanying elongation (orientation) of a polymer chain. First, we will derive the results for a simple dumbbell model and then generalize it to a more realistic freely jointed chain model (assuming, however, that the elongation occurs homogeneously along the chain). The orientation distribution function for chain segments will be calculated. Then, we will obtain an expression for the association constant in the presence of an external flow field for ''linear'' associated chains as well as for T-polymers and finally, we will discuss mixtures where ''linear,'' T-polymers, as well as complex linear/T-polymers can be formed.

II. MODEL

We will consider a solvent-free binary mixture of homopolymers A and B. For the first case considered, each polymer (A and B) carries an associative group at one of its ends, allowing only ''linear'' $A-B$ complex formation (Fig. 1). The chemical nature and length of the A- and B-polymer can be different, but we will assume that the hydrodynamic resistance of the segments is the same for both chains. Furthermore, the chain lengths are assumed to be smaller than the characteristic entanglement length N_e. The association is assumed to take place via orientationally dependent interactions, such as hydrogen bonding. If the value of the angle between the two segments next to the donor and acceptor groups, φ, (Fig. 1) is larger than some critical value Δ no bond can be formed. The value of this critical angle depends on the nature of the donor and acceptor groups. (In average[9] for hydrogen bonding this value is of the order of $3\pi/4$.) Besides the formation of ''linear'' polymer chains via single association of two homopolymers, we will discuss also the

influence of chain architecture on the association rate constant, e.g., the formation of associated T-polymers.

The association constant is in fact a quasiequilibrium quantity since formation/rupture of hydrogen bonds (or other type of reversible bonds) is a fast process which is practically independent of the sample history. As we will show below, the association constant depends strongly on the chain extension. The latter can of course depend on the history of the sample, however as long as we deal with elastic (reversible) deformations and relatively short polymer chains (with $N < N_e$) characterized by quick relaxation kinetics, ''history'' effects can be neglected and the polymer system under elongational flow can be modelled as a quasiequilibrium system experiencing the influence of an external potential field. Of course, such treatment has a limited applicability since it cannot be applied to nonpotential flows such as shear flow. However, this simple approach provides information about the most general qualitative features of associating polymer blends which may serve as a starting point for understanding of associating (hydrogen bonding) polymer systems subjected to shear flow.

For a three-dimensional elongational flow with longitudinal gradient

$$v_o = \gamma(-x/2, -y/2, z) \tag{1}$$

the external potential $U(\theta, r)$ acting on a polymer chain of N monomer units (Kuhn segments) has the form[26]

$$U(\theta, r) = \frac{\Phi(\theta, r)}{D} \simeq \frac{\gamma r^2 N \xi}{4kT}(1 - 3\cos^2 \theta), \tag{2}$$

where D is the diffusion coefficient for a chain $D \simeq kT/N\zeta$,[62] and ζ is the friction coefficient per monomer unit (segment), which is supposed to be the same for both chains. In Eq. (2) we have taken into account that the potential $U(\theta, r)$ is connected (through the hydrodynamic resistance of a chain to the flow) with the scalar potential $\Phi(v_o = -\nabla\Phi)$,

$$\Phi = \frac{\gamma r^2}{4}(1 - 3\cos^2 \theta). \tag{3}$$

Because of the symmetry created by elongational flow, spherical coordinates [$x = r \cos \psi \sin \theta$, $y = r \sin \psi \sin \theta$, $z = r \cos \theta$, θ being the angle between the direction along the chain and the flow direction (z axis)] are the obvious choice to characterize the behavior of the polymer system.

We will start our analysis by considering the chain elongation due to the external elongational (flow) field. First we will ''justify'' our approach based on a free energy analysis by considering a simple dumbbell model of a polymer chain, deriving the well known result for the orientation distribution function obtained before by Peterlin by solving the diffusion equation.[54] Then, we will generalize this approach to the freely jointed model (in the limit of homogeneous elongation) and use these results for the analysis of the association properties.

A. Dumbbell model

In the dumbbell model a polymer chain is described as an elastic dumbbell with length equal to the radius of gyration of the chain, R. A melt of dumbbells can be treated in a

similar way as a melt of liquid crystalline polymers.[63–66] The polymer chain (dumbbell) is characterized by the distribution function $P(\theta,R)$ denoting the probability to find a chain with radius of gyration R oriented at angle θ with respect to the z axis

$$\int P(\theta,R)dV = 1. \tag{4}$$

This distribution function can be derived from a free energy analysis. The free energy (per polymer chain) in the presence of the external (flow) field can be presented in the form

$$f = f_{orient} + f_{flow} + f_{el}, \tag{5}$$

where f_{orient} is the free energy describing the entropy loss due to orientation (elongation), f_{flow} is the free energy connected with the external field, and f_{el} is the elastic free energy. In Eq. (5) we take into account only those terms that depend on $P(\theta,R)$.

As for liquid crystalline polymers,[63–66] the free energy accounting for the entropy loss due to chain orientation and elongation, f_{orient}, can be written in the form

$$f_{orient} = \int P(\theta,R)\ln[C_o P(\theta,R)]dV, \tag{6}$$

where C_o is the normalization coefficient (which will be discussed further on). The free energy f_{flow} connected with the external orientational potential field $U(\theta)$, has the form[63–66]

$$f_{flow} = \int P(\theta,R)U(\theta,R)dV. \tag{7}$$

The elastic free energy, f_{el}, can be presented as

$$f_{el} = \int \frac{3}{2}E(\bar{Y})\frac{R^2}{R_o^2}P(\theta,R)dV, \tag{8}$$

where $Y \equiv R/L$ is the extension ($L=Nl$ is the contour length of the polymer chain) and $E(Y)$ is defined by

$$E(Y) = \frac{\mathcal{L}^{-1}(Y)}{3Y} \sim \begin{cases} 1+3Y^2/5+\dots & Y\to 0 \\ 1/3Y(1-Y) & Y\to 1, \end{cases} \tag{9}$$

where $\mathcal{L}^{-1}$ is the inverse Langevin function [$\mathcal{L}(u) = \coth(u) - 1/u$]. In Eq. (8) the standard assumption that E depends only on the average radius of gyration $\bar{R}$, is applied.

Minimization of the free energy Eq. (5) with respect to the distribution function $P(\theta,R)$ in the absence of flow results in the standard Gaussian function

$$P(\theta,R) = \left(\frac{3E}{2\pi}\right)^{3/2} R_o^{-3} \exp\left(-\frac{3E}{2}\frac{R^2}{R_o^2}\right), \tag{10}$$

where R_o is the average radius of gyration for a Gaussian chain ($=N^{1/2}l$). The distribution function is obviously independent of angle variables. Hence, in the absence of flow the polymer chain has a Gaussian conformation (as is expected for melts), $f_{el}+f_{orient}=0$ and the normalization coefficient C_o is equal to $(2\pi R_o^2/3E)^{3/2}$.

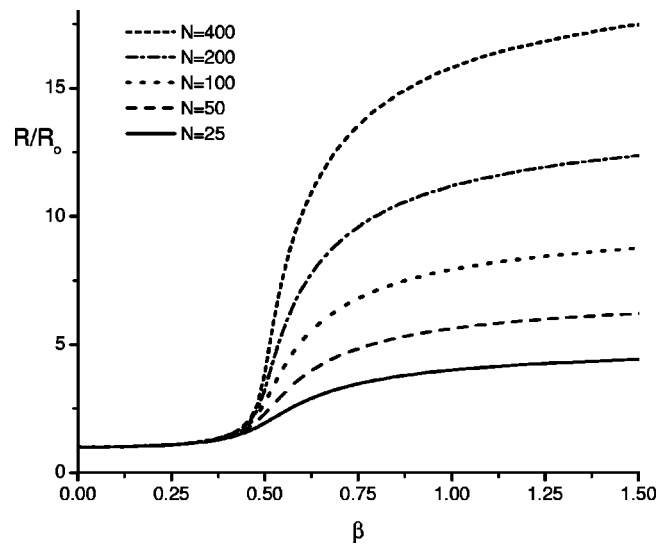In the presence of an elongational flow field the result of the free energy minimization is

FIG. 2. Extension $\bar{R}/R_o$ vs flow rate for polymer chains of different length.

$$P(\theta,R) = \left(\frac{3E}{2\pi R_o^2}\right)^{3/2}\left(1+\frac{\beta}{E}\right)\left(1-2\frac{\beta}{E}\right)^{1/2}$$
$$\times \exp\left\{-\frac{3E}{2R_o^2}R^2 - \frac{\gamma R^2}{4D}(1-3\cos^2\theta)\right\}, \tag{11}$$

where

$$\beta = \frac{\gamma R_o^2}{6D} = \gamma \frac{\zeta l^2}{6kT}N^2 \tag{12}$$

is the dimensionless parameter accounting for both the flow rate and the characteristic chain relaxation time (chain resistance to the flow).

Integration over all possible values of the radius of gyration gives the distribution function $P(\theta)$ depending on chain orientation only

$$P(\theta) \equiv \int P(\theta,R)R^2 dR$$
$$= \frac{1}{4\pi}(1+\beta/E)(1-2\beta/E)^{1/2}$$
$$\times [1+\beta(1-3\cos^2\theta)/E]^{-3/2}. \tag{13}$$

The average radius of gyration for a polymer chain subjected to flow can also be obtained from the orientation distribution function

$$\bar{R^2} = \int R^2 P(\theta,R)dV = R_o^2\frac{(E-\beta)}{(E+\beta)(E-2\beta)}. \tag{14}$$

The chain extension $\bar{R}/R_o$ is presented in Fig. 2 as a function of flow rate β. The chain extension depends strongly on both chain length and flow rate. The stronger the flow rate, the larger the extension. Furthermore, for a given flow rate longer polymer chains turn out to be more elongated (and oriented) than shorter chains. This effect plays an essential role in the process of chain association as we will see below.

As expected, the results for the chain distribution function [Eq. (11)] and the average end-to-end distance [Eq. (14)] reproduce the results of Peterlin[54] for the dumbbell model obtained by solving a diffusion equation [Eq. (7) in Ref. 54]. This fact confirms that the free energy analysis applied is effective in describing quasiequilibrium steady state properties of a polymer system under flow, which strictly speaking is a kinetic rather than a thermodynamic problem.

B. Orientation distribution function for a freely jointed chain

In the previous section we obtained the distribution function and estimated the extension for the polymer chain as a whole by treating the chain as a dumbbell with end-to-end distance equal to the radius of gyration (along the principal axis of the chain) of the real chain. This model is suitable for studying the overall characteristics of the chain, but it cannot provide the details of the chain conformations necessary for an accurate analysis of the association properties. To get information about the local orientation of chain segments, a more detailed model of a polymer chain such as the freely jointed model (with a segment length equal to the Kuhn length l of the real chain) is required.

We can write the free energy [depending now on the segment distribution function $P_{seg}(\theta)$] as

$$F_{fj} = f_{field}^* + f_{orient}^*, \tag{15}$$

where f_{field}^* describes the elastic free energy connected with the action of the external potential (flow) field and f_{orient}^* is the free energy accounting for the entropy loss due to chain orientation and elongation.

The influence of flow on the orientation of chain segments is rather complex and manifests itself mainly in an indirect way. Indeed, if we would be dealing with a blend of disconnected segments the potential acting on segments could be written as before: $U_{flow}^* = (\gamma l^2 \xi / 4kT)(1 - 3\cos^2 \theta)$. For segments jointed into a chain, the potential is obviously different. Under the influence of flow the polymer chain becomes oriented and elongated. The chain stretching (orientation) occurs actually through segment orientation.[67] Hence, the orientational potential experienced by each segment of the freely jointed chain is in fact defined by the stretching force (being in equilibrium with an elastic force) acting on the chain as a whole. Since chain stretching occurs inhomogeneously (the middle of the chain being more stretched than the chain tails),[57] the potential may also depend on the position of a segment along the chain.

However, since we are mainly interested in chain averaged characteristics of segments, we shall make some simplifying assumptions. First, we will neglect the effect of inhomogeneity of the chain extension which will make the orientation function independent of the position of a segment along the chain. (This assumption is similar to the affine deformation approximation in the theory of viscoelasticity, i.e., it may work reasonably well only for small stress and hence deformations, $Y \ll 1$). Second, instead of considering the potential for each individual chain (having radius of gyration R) and further averaging over all possible segment orientations, we will make a ''mean-fieldlike'' approxima-

tion assuming that there is some average potential acting on the segments of all chains of the same length independent of the conformation of the chain. (The limitations inflicted by this approximation will be discussed later.) This averaged potential is actually the potential acting on the segments of a chain with average radius of gyration $\bar{R}$ at steady state. The value of the steady state radius of gyration $\bar{R}$ (or the extension Y for a chain) can be estimated from analytical considerations such as Eq. (14) or taken from experimental data. In the case of elongational flow stretching occurs mainly in flow (z) direction. The maximal orientational potential is experienced by a segment with orientation perpendicular to flow while no orientational field is acting on a segment aligned along the flow

$$U_{st} = f_{chain} l (1 - \cos \theta)$$

$$= 3\frac{\bar{R}E(\bar{R})}{R_o^2} l (1 - \cos \theta)$$

$$= \alpha(1 - \cos \theta) \quad \text{for } 0 \leq \theta \leq \pi/2, \tag{16}$$

$$U_{st} = \alpha(1 + \cos \theta) \quad \text{for } \pi/2 \leq \theta \leq \pi \tag{17}$$

with

$$\alpha = 3\frac{\bar{R}E(\bar{R})}{L} \equiv 3\bar{Y}E, \tag{18}$$

where f_{chain} is the stretching force being in equilibrium with an elastic force. (Strictly speaking, if the chain is relatively short then there is an ''initial stretching potential'' $U_{st}^0 \sim R_o/L \sim N^{-1/2}$. In this case to define the potential due to flow effects only, we should consider the difference $\Delta U_{st} = U_{st} - U_{st}^0$.)

It is worth while to emphasize that the dependence of the potential on the flow rate is included in the values of $\bar{R}$ and $E(\bar{R})$ assuming that there is a direct dependence between the flow rate γ and the steady state radius of gyration $\bar{R}$. Of course, in reality some hysteresis effect may take place and a polymer chain recovering after experiencing strong flow can have a larger radius of gyration than during the ''direct'' elongation by flow. Since association occurs very quickly (i.e., the characteristic time for association/dissociation is much smaller than the characteristic relaxation time for a chain) the association rate will be dependent (in our approximation) on the steady state chain extension rather than on the real flow rate.

Thus, the contribution to the free energy connected with the chain extension is given by

$$f_{field}^* = N \int P_{seg}(\theta) U_{st}(\theta) d\Omega. \tag{19}$$

The free energy accounting for the entropy loss of a chain of N freely jointed segments due to chain orientation and elongation, f_{orient}^*, can be written in the form[63–65]

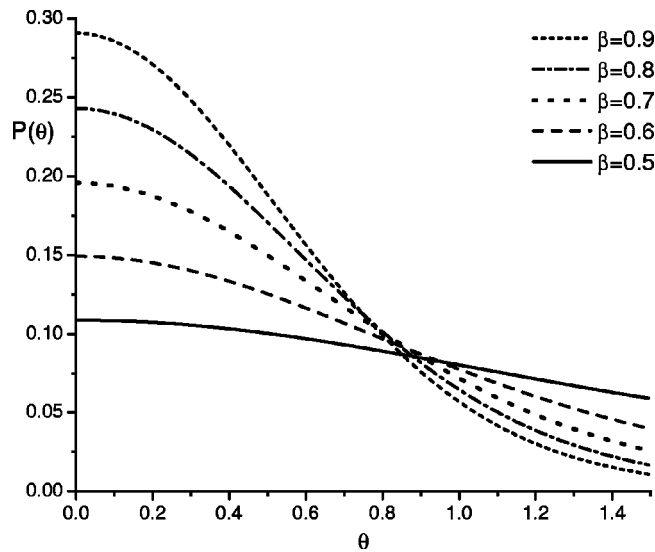$$f_{orient}^* = N \int P_{seg}(\theta) \ln[4\pi P_{seg}(\theta)] d\Omega. \tag{20}$$

FIG. 3. Orientation distribution function for segments of chain containing 25 segments at different flow rates.

FIG. 4. Orientation distribution function for segments of chains of different length at flow rate $\beta/N^2 = 0.001$.

Minimization of the free energy taking into account the normalization condition for $P_{\text{seg}}(\theta)$ $[\int P_{\text{seg}}(\theta)d\Omega = 1]$ leads to the following expressions for $P_{\text{seg}}(\theta)$:

$$P_{\text{seg}}(\theta) = \frac{1}{4\pi} \frac{\alpha}{(\exp\alpha - 1)} \exp(\alpha\cos\theta) \quad \text{for } 0 \leq \theta$$

$$\leq \pi/2,$$

$$P_{\text{seg}}(\theta) = \frac{1}{4\pi} \frac{\alpha}{(\exp\alpha - 1)} \exp(-\alpha\cos\theta)$$

$$\text{for } \pi/2 \leq \theta \leq \pi. \tag{21}$$

For strong flow, when $\alpha \gg 1$, $P_{\text{seg}}(\theta)$ assumes the Gaussian form[66]

$$P_{\text{seg}}(\theta) = \frac{\alpha}{4\pi}\exp\left(-\frac{\alpha}{2}\theta^2\right) \quad \text{for } 0 \leq \theta \leq \pi/2,$$

$$P_{\text{seg}}(\theta) = \frac{\alpha}{4\pi}\exp\left(-\frac{\alpha}{2}(\pi-\theta)^2\right) \quad \text{for } \pi/2 \leq \theta \leq \pi. \tag{22}$$

The normalization of the latter expressions is not exact, the prefactor $\alpha/4\pi$ should actually be $\alpha/4\pi[1 - \exp(-\pi^2\alpha/8)]$, i.e., exponentially small terms have been omitted.

The orientation distribution function $P_{\text{seg}}(\theta)$ is shown in Fig. 3 for different flow rates. With increasing flow rate the polymer chain assumes a more extended conformation (Fig. 2) implying a stronger orientation for the chain segments. As discussed above, the assumptions made do not allow us to predict explicitly the orientation distribution function for segments, rather it gives an average picture of their alignment along the flow.

The influence of chain length on the orientation distribution function for segments is illustrated in Fig. 4. Intuitively one might expect the segment orientation of longer chains to be somewhat smaller than that for shorter chains, since segments of longer chains obviously have more freedom to assume any orientation compatible with the overall chain end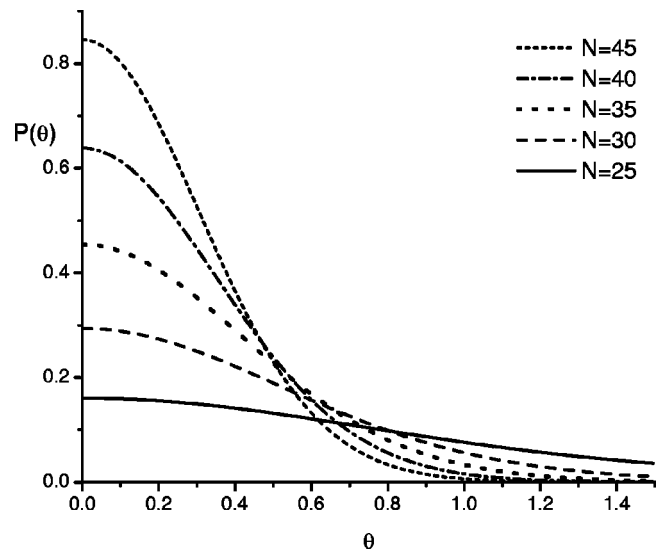-to-end distance and orientation. However, longer polymer chains turn out to be elongated to a much larger extent than shorter chains, which actually leads to a stronger orientation of segments belonging to a long chain compared to a short chain.

The increase of the free energy (per segment) under flow can be estimated through the entropy loss for segment orientation {by substitution of $P_{\text{seg}}(\theta)$ [Eqs. (21),(22)] into the free energy Eq. (15) and dividing by N}:

$$\Delta f_{\text{seg}} = \ln\{\alpha/[1 - \exp(-\alpha)]\}$$

$$\simeq \begin{cases} \ln(1+\alpha) \simeq \alpha & \text{for } \alpha \to 0 \\ \ln\alpha & \text{for } \alpha \gg 1. \end{cases} \tag{23}$$

While for the Gaussian form of $P_{\text{seg}}(\theta)$ this is

$$\Delta f_{\text{seg}} = \ln\{\alpha/[1 - \exp(-\alpha\pi^2/8)]\} \simeq \ln\alpha \quad \text{for } \alpha \gg 1. \tag{24}$$

The dependence on chain length and flow rate is included via parameter α [Eq. (18)].

III. ASSOCIATION UNDER ELONGATIONAL FLOW

In the absence of an external flow field the free energy of a mixture of polymers associating via a reversible orientationally dependent interaction can be presented in the form

$$F_o = (\mathcal{N}_A - \mathcal{N}_{AB})\ln\frac{(\mathcal{N}_A - \mathcal{N}_{AB})v}{eV}$$

$$+ (\mathcal{N}_B - \mathcal{N}_{AB})\ln\frac{(\mathcal{N}_B - \mathcal{N}_{AB})v}{eV} + \mathcal{N}_{AB}\ln\frac{\mathcal{N}_{AB}v}{eV}$$

$$+ \chi N_A N_A \frac{\mathcal{N}_B N_B v}{V}$$

$$- \int\int \mathcal{N}_{AB}(\theta,\psi,\theta',\psi')F_{AB}(\theta,\psi,\theta',\psi)d\Omega d\Omega', \tag{25}$$

where $\mathcal{N}_A$, $\mathcal{N}_B$, and $\mathcal{N}_{AB}$ are the number of free polymer chains of kind A, B, and hydrogen bonded AB-chains and v is the volume per monomer unit.

The first three terms in Eq. (25) correspond to the translational entropy of free A-chains, free B-chains, and hydrogen bonded AB-chains, respectively. The fourth term describes the volume interactions in the system with χ the Flory–Huggins interaction parameter. The last term in Eq. (25) is related to the free energy change due to orientational dependent association (hydrogen bonding). As discussed above, the free energy of association strongly depends on the orientation of donor and acceptor groups, hence, in general it is a function of these angles, $F_{AB}(\theta,\psi,\theta',\psi')$. The number of corresponding hydrogen bonded chains (having ''donor segment'' oriented at angles θ and ψ, and ''acceptor segment'' oriented at angles θ' and ψ') is denoted by $\mathcal{N}_{AB}(\theta,\psi,\theta',\psi')$. The total number of hydrogen bonded chains in the system is

$$\mathcal{N}_{AB}=\int\int \mathcal{N}_{AB}(\theta,\psi,\theta',\psi')d\Omega d\Omega', \qquad (26)$$

where $d\Omega(d\Omega')$ is an element of space angle related to angles θ, ψ (θ',ψ').

In the presence of an external elongational (flow) field, the free energy of the system can be written as

$$F=F_o+(\mathcal{N}_A-\mathcal{N}_{AB})F^A_{fj}+(\mathcal{N}_B-\mathcal{N}_{AB})F^B_{fj}+\mathcal{N}_{AB}F^{AB}_{fj}, \qquad (27)$$

where F_o is the free energy of the mixture in the absence of flow [Eq. (25)] and F^I_{fj} is the free energy of a freely jointed chain of sort $I(I=A,B,AB)$ under external flow, discussed in Sec. II [Eq. (15)]. The free energy of a mixture of associating polymers under flow is a complex function of the number density of associated chains and the orientation distribution functions for segments (contributing F^I_{fj}). Since these variables can be considered as independent ones, the minimization will lead to a set of decoupled equations for the orientation distribution functions for segments of free A-chains, free B-chains, and associated AB-chains, except for the segments next to the donor/acceptor groups of the associated chains. The orientation distribution function for these segments is coupled with the number of associated chains through the free energy per association $F_{AB}(\theta,\psi,\theta',\psi')$. The orientation distribution functions for segments of free A-chains, free B-chains, and associated AB-chains (except for the segments next to the donor/acceptor groups) are described by Eqs. (21) and (22). It is important to remember that the parameter α characterizing the degree of segment orientation depends on the steady state radius of gyration (extension) of the chains, and hence, it is different for chains of different length at the same flow rate or for the same chains at different flow rates.

As we discussed above, the effective free energy approach has limited applicability as it can be used only for potential flows. In addition, the approach cannot be applied when there are strong fluctuations in the velocity field about the average flow. Therefore we cannot expect our model to work well for the polymer blends with a large fraction of long chains (original or associated) under strong flow. Nei-

ther the strong fluctuations created by the flow nor the involvement of shorter chains in the stretching process experiencing by the longer chains can be accounted in a proper way in the framework of the present approach. Thus, we will mainly deal with the polymer blends with a dominant fraction of short chains (which can be considered as an oligomer solvent) under relatively weak flow, $\gamma\tau\equiv\beta<1$, where our model is expected to work the best.

Minimization of the free energy F with respect to the fraction of associated polymer chains $\mathcal{N}_{AB}$ leads to the following equation

$$\frac{\mathcal{N}_{AB}}{V}=K_{\mathrm{ass}}\frac{(\mathcal{N}_A-\mathcal{N}_{AB})}{V}\frac{(\mathcal{N}_B-\mathcal{N}_{AB})v}{V}$$

$$\times\int\int\exp\{F_{AB}(\theta,\psi,\theta',\psi')\}P^{AB}_{\mathrm{seg}}(\theta)P^{AB}_{\mathrm{seg}}(\theta')d\Omega d\Omega', \qquad (28)$$

where we use the results of minimization over the orientation distribution function for segments of free A-chains, free B-chains, and associated AB-chains (except for segments next to donor/acceptor groups of associated chains).

In Eq. (28) we have introduced the association constant K_{ass} which characterizes the influence of flow on the association of polymers resulting from the difference in extension rates for associated and nonassociated polymers

$$K_{\mathrm{ass}}=\exp[N_A\Delta f^A_{\mathrm{seg}}+N_B\Delta f^B_{\mathrm{seg}}-(N_A+N_B)\Delta f^{AB}_{\mathrm{seg}}], \qquad (29)$$

where $\Delta f^I_{\mathrm{seg}}$ is the free energy loss per elongation (orientation) of a polymer chain of sort $I(I=A,B,AB)$. An expression for $\Delta f^I_{\mathrm{seg}}$ has been calculated in the previous section, Eqs. (23) and (24).

For orientationally independent association $[F_{AB}(\theta,\psi,\theta',\psi')=\mathrm{const}]$ the influence of the external flow field is described entirely by the association constant K_{ass}. In the absence of flow $K_{\mathrm{ass}}=1$. If the segment orientation (or chain extension) for associated chains would have been the same as that for the nonassociated homopolymer chains, there would be no additional factors influencing the association. However, as discussed in the previous section, at the same flow rate the segment orientation and elongation of longer polymer chains is considerably stronger than that of shorter chains. Consequently, the penalty for segment orientation (and chain elongation) of an associated chain exceeds that of the two initial homopolymer chains, which leads to a decrease of the association constant in comparison to the initial state (in the absence of flow).

The dependence of the association constant K_{ass} on the flow rate (β/N^2_I) is presented in Fig. 5 for several binary mixtures of homopolymer chains of different length, all leading to formation of associated chains of the same length. The minimum value of K_{ass} corresponds to a mixture of homopolymers of the same length $N_A=N_B=50$. For a mixture of homopolymers of similar length, i.e., $N_A\simeq N_B$, the associated chain is twice as large as the original chains and there is a considerable entropy loss for all N_A+N_B segments. In the same picture the extension for associated and nonassociated chains with $N_A=N_B=50$ is presented as well. A comparison of the chain extension shows that the associated
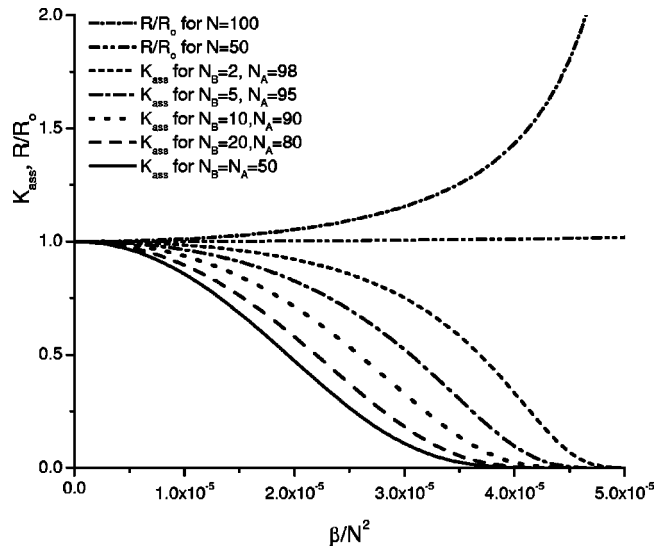
FIG. 5. K_{ass} and extension $\bar{R}/R_o$ for polymer mixtures of different composition (with length of associated chains $N_A+N_B=100$) vs flow rate β/N^2.

chains become already considerably stretched at flow rates where the original homopolymer chains are still practically unperturbed by the flow. As a result, each segment of the associated chain loses entropy and the association constant K_{ass} decreases rapidly as the associated chain adopts a stretched conformation. Since under elongational flow the transition of the chain to a practically completely stretched conformation occurs in a relatively narrow flow rate interval, the association constant K_{ass} also decreases steeply (to practically zero) in a relatively small range of flow rates.

The larger the difference in length of the homopolymer chains, the larger the association constant K_{ass} (Fig. 5). The physical reason for this effect is clear. If the length of one chain is much smaller than that of the other, e.g., $N_B \ll N_A$, the associated chain will be only slightly larger than the A-chain. Hence, the entropy loss due to additional orientation (and chain elongation) will be large only for the N_B segments of the associated chain, while the N_A segments will lose only a relatively small amount of entropy.

When the strength of the association depends on the mutual orientation of donor and acceptor groups, there is an additional $F_{AB}(\theta,\psi,\theta',\psi')$ dependent factor in Eq. (28). In general $F_{AB}(\theta,\psi,\theta',\psi')$ changes smoothly with the mutual orientation of the donor and acceptor groups. However, since the functional dependence is influenced strongly by the nature of the hydrogen bond and is different for different types of donor–acceptor groups, we will assume a simple step-like function

$$F_{AB}(\theta,\psi,\theta',\psi') = \begin{cases} \dfrac{H}{T} & \text{if } \varphi \leqslant \Delta \\[2mm] 0 & \text{if } \varphi > \Delta, \end{cases} \tag{30}$$

i.e., we will assume an equal probability of hydrogen bond formation if the angle between donor and acceptor group, φ, is smaller than Δ and no hydrogen bonding otherwise. Then Eq. (28) can be rewritten in the following form:

$$\frac{\mathcal{N}_{AB}}{V} = K \frac{(\mathcal{N}_A - \mathcal{N}_{AB})}{V} \frac{(\mathcal{N}_B - \mathcal{N}_{AB})v}{V}; \quad K \equiv K_o K_{\mathrm{ass}} K_{\mathrm{or}}, \tag{31}$$

where

$$K_{\mathrm{or}} = \int \int_{\varphi \leqslant \Delta} P_{\mathrm{seg}}^{AB}(\theta) P_{\mathrm{seg}}^{AB}(\theta') d\Omega d\Omega', \tag{32}$$

$$K_o = \exp(H/T). \tag{33}$$

In the absence of an external (flow) field the orientation of segments is isotropic, $P_{\mathrm{seg}}^{AB}(\theta) = 1/4\pi$. Then, the integral Eq. (32) is

$$K_{\mathrm{or}}^o = \frac{1-\cos\Delta}{2}. \tag{34}$$

If $\Delta = \pi$, i.e., the association is angle independent, $K_{\mathrm{or}}^o = 1$. In the opposite limit, when association is possible only in the very narrow angle range $\Delta \to 0$, the probability of association becomes very small $K_{\mathrm{or}}^o \simeq \Delta^2/4 \to 0$.

Since in the absence of an external flow field $K_{\mathrm{ass}}=1$, the association constant is defined by the product $K_o K_{\mathrm{or}}^o$, i.e.,

$$K|_{\gamma=0} = K_o K_{\mathrm{or}}^o = \frac{1-\cos\Delta}{2} \exp(H/T). \tag{35}$$

A dependence of hydrogen bonding on the mutual orientation of donor and acceptor groups implies an entropy loss upon hydrogen bonding, S [cf. Eqs. (4) and (9) of Ref. 11]. The physical reason is that for polymer chains to be hydrogen bonded their segments next to the donor and acceptor groups should keep the correct orientation with respect to each other. In Eq. (31) the entropy loss for hydrogen bonding is accounted for by K_{or}, which is just another form of describing the same physical effect. So that the entropy loss S for hydrogen bonding, used as a parameter in our previous papers,[11,12] depends on the nature of hydrogen bonding through the value of the critical angle Δ as

$$S = -\ln K_{\mathrm{or}}. \tag{36}$$

In the absence of flow, when $K_{\mathrm{or}} = K_{\mathrm{or}}^o$, the entropy loss S is defined by the value of the critical angle Δ only and the fraction of hydrogen bonded chains, $X = \mathcal{N}_{AB}/\mathcal{N}_A$, depends strongly on Δ.

K_{or} characterizes the influence of flow on the association constant K, resulting from the change in probability to find a donor–acceptor pair at correct orientation for hydrogen bonding. As discussed above, $P_{\mathrm{seg}}^{AB}(\theta)$ is strongly dependent on the flow rate and length of the polymers. As a result, K_{or} and correspondingly the entropy loss for hydrogen bonding, S, varies with flow rate. K_{or} can be calculated numerically, but in order to find analytical expressions for K_{or} in the limit of weak and strong flow we will consider only the limit of very small Δ, where the influence of the orientational dependence on the association rate will be maximal, and the opposite limit when the characteristic angle is close to $\pi - \delta$ ($\delta \ll 1$) and hydrogen bonding is almost orientationally independent.
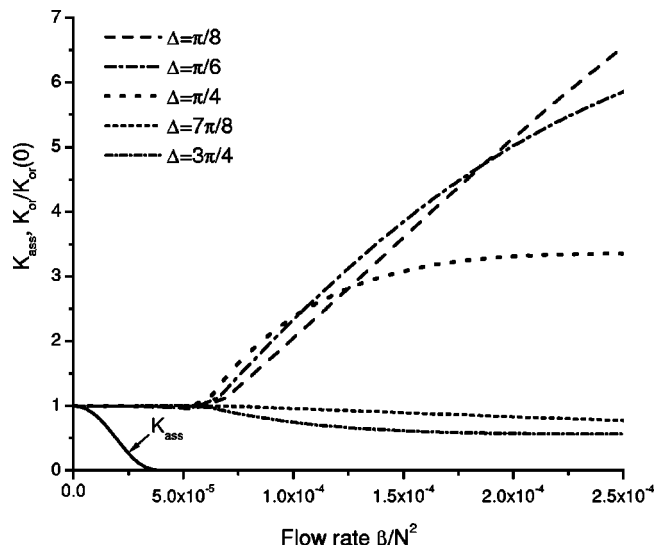
FIG. 6. The association constant vs flow rate for hydrogen bonded mixture ($N_A = N_B = 50$). K_{ass} is the association constant accounting for extra-stretching of the associated chain (compared with the two initial chains). $K_{or}/K_{or}(0)$ is the association rate constant accounting for the orientational dependence of hydrogen bonding, presented for different values of critical angle Δ.

In the limit of weak flow $\alpha_{AB} \ll 1$ [where α_{AB} for associated chain is defined by Eq. (18)] and small Δ ($\Delta < \pi/2$), K_{or} can be estimated as

$$K_{or} \simeq \frac{\Delta \sin \Delta}{\pi} \left(\frac{\alpha_{AB}}{\exp(\alpha_{AB}) - 1} \right)^2 \left\{ \frac{\pi}{4} - \frac{\Delta}{2} + \frac{\sin 2\Delta}{4} \right.$$

$$\left. + \frac{\alpha_{AB}}{3} (1 + \cos \Delta)(1 - \sin^3 \Delta) + O(\alpha_{AB}^2) \right\}$$

$$+ \frac{1}{2} \left[\frac{1 - \exp[-\alpha_{AB}(1 - \cos \Delta)]}{1 - \exp(-\alpha_{AB})} \right]^2. \tag{37}$$

In the limit $\alpha_{AB} \to 0$ and $\Delta \to 0$, $K_{or} \to \Delta^2/4$ in agreement with the behavior of K_{or}^o [Eq. (34)]. In the limit of large flow rates $\alpha_{AB} \gg 1$, K_{or} tends to the following value

$$K_{or} \simeq \frac{\Delta^2}{4} \sqrt{\frac{\alpha_{AB}}{\pi}} \exp\left(-\frac{\alpha_{AB}}{4} \Delta^2 \right)$$

$$+ \frac{1}{2} \left[1 - \exp\left(-\frac{\alpha_{AB}}{2} \Delta^2 \right) \right]^2. \tag{38}$$

It is worth while to note, however, that we can expect our results to be valid mainly for $\alpha < 1$ [or $Y < 1/(3E)$] since the averaged potential approximation (i.e., the assumption of similar stretching for all segments of the chains of the same length), which was applied for the calculation of the orientation distribution function for chain segments, holds only to first order in α. The condition, $\alpha < 1$, is in fact less restrictive than $\gamma\tau \equiv \beta < 1$.

The dependence of $K_{or}/K_{or}(0)$ on flow rate for a mixture of polymers of the same length $N_A = N_B = 50$ is presented in Fig. 6 for different values of the critical angle Δ. For $\Delta < \pi/2$ the association rate constant K_{or} increases with an increase of flow rate. The increase becomes pronounced mainly when the parameter α_{AB} exceeds 1, i.e., then the

associated chain becomes considerably stretched (however, in this limit our model may fail, as we discussed above). For very large flow rates $K_{or}/K_{or}(0)$ tends to a limiting value depending on Δ. In fact $K_{or} \to 1/2$ in this limit ($\alpha_{AB} \gg 1$, $\Delta \ll 1$) since this is the probability to find two chains oriented in the opposite directions when all polymer chains align along the flow. If hydrogen bonding has a weak orientational dependence, i.e., the characteristic angle is close to $\pi - \delta$, then $K_{or}(\pi - \delta) \simeq 1 - K_{or}(\delta)$ with $K_{or}(\delta)$ defined by Eqs. (37) and (38). $K_{or}(\pi - \delta)$ decreases with increasing flow rate, however, the relative decrease is not large compared to 1 [or compared to the value of $K_{or}(\pi - \delta)$ in the absence of flow].

The association constant K_{ass} (accounting for the decrease of the association due to extra stretching of a hydrogen bonded chain compared to the two initial homopolymer chains) is also presented in Fig. 6. A comparison between the behavior of K_{or} and K_{ass} shows that K_{ass} steeply decreases to a very small value as the hydrogen bonded chain becomes elongated, whereas K_{or} increases (for $\Delta < \pi/2$) gradually reaching relatively large values only at rather large flow rates. As a result, the product $K_{or}K_{ass}$ behaves practically the same as K_{ass}. The physical reason for this effect is the following. K_{ass} accounts for the extra orientation of all segments of the hydrogen bonded chain, while the effect of improvement of chain orientation for hydrogen bonding, described by K_{or}, is based only on the orientation of the two segments next to the donor and acceptor groups. Hence, K_{or} becomes large only when these two segments become strongly oriented, however, all other segments of the chain are also strongly oriented and K_{ass} is already very small. As a result, the influence of the orientational effect (K_{or}) on the total association rate turns out to be relatively small. The product $K_{ass}K_{or}/K_{or}(0)$ is indistinguishable from K_{ass} on the scale of Fig. 6 even though at large flow rates $K_{ass}K_{or}/K_{or}(0)$ may be 10 times as large as K_{ass} which, however, may become smaller than e^{-10} for chains with $N_{AB} \geq 100$. As discussed above, K_{ass} decreases relatively smoothly when the lengths of the homopolymers differ strongly. However, if one of the homopolymer chains is short, then the orientation of the segments of this chain will be relatively weak and the contribution of K_{or} to the total association constant K will still be relatively small.

The relative fraction of associated chains X (with respect to the initial number of A-chains) is given by (cf. Refs. 11 and 12)

$$X = \frac{\mathcal{N}_{AB}}{\mathcal{N}_A} = \frac{1}{2}\{A - [A^2 - 4X_B]^{1/2}\}, \tag{39}$$

$$A \equiv \frac{N_A}{K\Phi} + 1 + X_B,$$

where Φ is the volume fraction of A-polymers and $X_B \equiv \mathcal{N}_B/\mathcal{N}_A = (1/\Phi - 1)N_A/N_B$ is the relative fraction of B-chains. The temperature dependence of the average fraction of hydrogen bonded chains, X, in a mixture with a dominant fraction of B-chains ($N_A = N_B = 50$, $\Phi = 0.2$, $\Delta = 3\pi/4$, $H = 2500$ K) is presented in Fig. 7. Since the total association rate constant K decreases with increasing flow rate (in a simi-
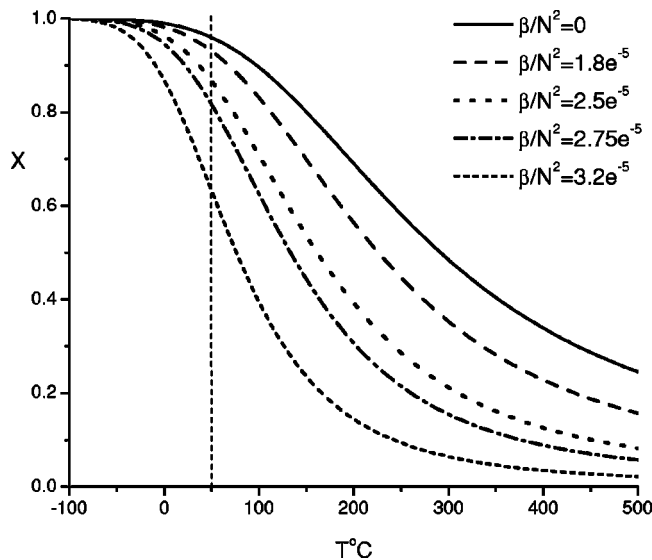
FIG. 7. Temperature dependence of the relative fraction of associated chains X for the polymer mixture ($N_A = N_B = 50$, $H = 2500$ K, $\Phi = 0.2$, $\Delta = 3\pi/4$) at several flow rates.

FIG. 8. Schematic picture of associated T-polymers (A) and complex linear/T-polymers (B).

lar way as K_{ass}), the fraction of hydrogen bonded chains also decreases. The decrease is most pronounced in the region of intermediate temperatures where the fraction of associated chains changes most rapidly with temperature. Besides the decrease of X, the temperature dependence $X(T)$ becomes less smooth, so that for large flow rates the fraction of hydrogen bonded chains changes dramatically in a relatively small temperature range. In the absence of flow such a strong change in the degree of association would strongly influence the phase behavior: a transition would be observed from a relatively stable state [corresponding to solid line of $X(T)$ dependence] to a much less stable state with respect to both macro and microphase separation with the possibility of a closed-loop two-phase region at elevated temperature. The phase diagram would be similar to that considered in Ref. 8. However, in the presence of flow the analysis of phase behavior is a much more complicated task (cf. Refs. 27, 32–34, 36, 37).

Associated polymers of different architecture. So far the formation of ''linear'' associated chain molecules was considered (Fig. 1). The architecture of associated chains studied experimentally is usually more complicated and frequently involves the formation of comb-like structures.[15] Below we will consider the simplest case of associated T-polymers where the perpendicular orientation between main chain and side chain is the preferred orientation [Fig. 8(A)]. Such a polymer is formed upon association of an A-polymer carrying one donor (or acceptor) group somewhere near the middle of the chain and a B-polymer with an acceptor (donor) group at one of its chain ends. T-polymers may have a larger tendency toward being entangled than ''linear'' polymers. Therefore, in the following we will consider mainly blends with a low fraction of long A-chains (and hence T-chains) in order to avoid dealing with entanglement effects. It is worth while to note that the short B-chains can be considered as oligomeric diluents which promotes disentanglement. Being a reversible association, hydrogen bond-
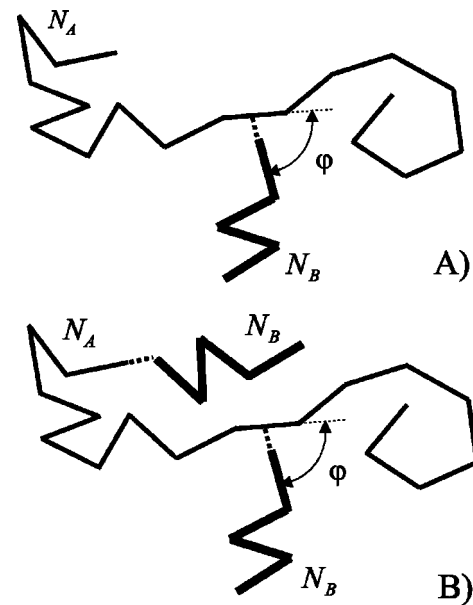
ing also hinders formation of strongly entangled structures as the stress associated with an entanglement can be relaxed via disruption of the hydrogen bond followed by its reformation when the chain becomes disentangled. Thus, we will consider the common situation where $N_A \gg N_B$ and $\Phi < 0.5$. Then, it is natural to expect that upon association the total radius of gyration for the associated AB-chain remains practically the same as for the A-chain. This means that in fact no extra-stretching takes place for the associated chain, compared to the two initial chains: the orientation of segments in both A- and B-blocks of the hydrogen bonded chain remains practically the same as for the initial chains. Hence, $K_{ass} \simeq 1$ for the hydrogen bonded T-polymers. The equation for the association constant for this case

$$\frac{\mathcal{N}_{AB}}{V} = K_o K_{or}^T \frac{(\mathcal{N}_A - \mathcal{N}_{AB})}{V} \frac{(\mathcal{N}_B - \mathcal{N}_{AB})v}{V} \tag{40}$$

can be obtained in a similar way as Eqs. (28) and (31), i.e., by minimization of the free energy Eq. (27), assuming that

$$F_{AB}(\theta, \psi, \theta', \psi') = \begin{cases} \dfrac{H}{T} & \text{if } \left| \dfrac{\pi}{2} - \varphi \right| \leqslant \Delta \\[2mm] 0 & \text{if } \left| \dfrac{\pi}{2} - \varphi \right| > \Delta \end{cases} \tag{41}$$

and taking into account that now the orientation distribution function for $A(B)$ segments of associated AB-chain is similar to that of nonassociated homopolymer $A(B)$ chain and

$$K_{or}^T = \int \int_{|\pi/2 - \varphi| \leqslant \Delta} P_{seg}^A(\theta) P_{seg}^B(\theta') d\Omega d\Omega'. \tag{42}$$

The association constant accounting for the effect of orientational dependence of hydrogen bonding K_{or}^T can be estimated in the limit of small Δ and $\alpha_B \leqslant \alpha_A < 1$ in a similar way as K_{or} [Eq. (37)]
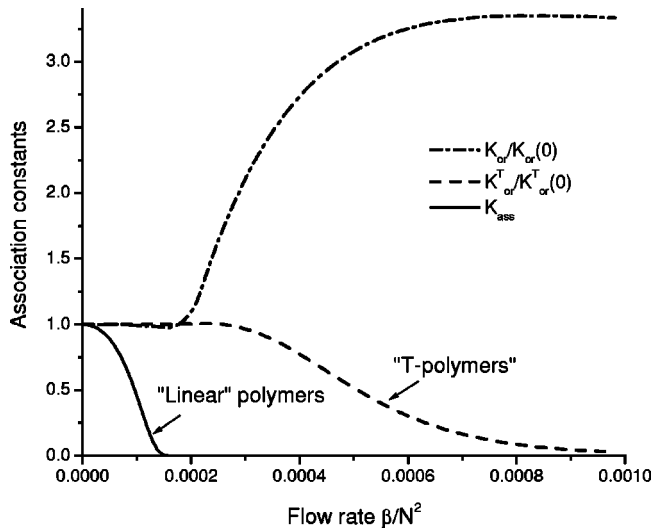
FIG. 9. The association constants vs flow rate for the associating mixtures ($N_A = 50$, $N_B = 5$, $\Delta = \pi/4$) with different architecture of associated chains. K_{ass}, $K_{or}/K_{or}(0)$ are the association constants for the mixture with ''linear'' associated chains (Fig. 1). $K_{or}^T/K_{or}^T(0)$ is the association constant for the mixture with T-chains [Fig. 8(A)].

$$
K_{or}^T \simeq \frac{\Delta \sin \Delta}{\pi} \left(\frac{\alpha_A}{\exp(\alpha_A) - 1} \right) \left(\frac{\alpha_B}{\exp(\alpha_B) - 1} \right) \left\{ \frac{1}{2} \cos^2 \Delta \right.
$$
$$
+ \frac{\alpha_A}{3} (1 - \sin^3 \Delta) - \frac{\alpha_B}{3} \cos^4 \Delta + O(\alpha^2) \right\}
$$
$$
+ \frac{1}{2} \left[\frac{1 - \exp[-\alpha_B(1 - \cos \Delta)]}{1 - \exp(-\alpha_B)} \right]
$$
$$
\times \left[\frac{\exp(\alpha_A \sin \Delta) - 1}{1 - \exp(-\alpha_A)} \right] \exp(-\alpha_A). \tag{43}
$$

In the absence of flow, when the distribution of the chain over space angles is isotropic, K_{or}^T is obviously defined by the same Eq. (34) as for ''linear'' hydrogen bonded polymers. At relatively large flow rates K_{or}^T decreases as $\exp(-\alpha_A)$.

The association constant $K_{or}^T/K_{or}^T(0)$ for hydrogen bonded T-polymers together with K_{ass} and $K_{or}/K_{or}(0)$ for linear hydrogen bonded chains formed in binary mixtures of homopolymers of the same composition ($N_A = 50$, $N_B = 5$, $\Delta = \pi/4$), with A-chains carrying a functional group either at the middle or at the end of the chain, are presented in Fig. 9. As discussed above, the product of $K_{ass} K_{or}/K_{or}(0)$ for ''linear'' AB-chains is indistinguishable from K_{ass} for the scale used. For T-polymers $K_{ass} = 1$ and the influence of the external (flow) field is described entirely by K_{or}^T. The association rate constant K_{or}^T decreases due to the decrease of the probability to find a donor–acceptor pair for hydrogen bonding at a correct orientation. Indeed, at large flow rates both A- and B-chains tend to align along the same direction (flow direction), which diminishes the probability to find a pair with perpendicular mutual orientation. A comparison between $K_{ass} K_{or}/K_{or}(0)$ and K_{or}^T shows that the latter is larger and decreases more smoothly. The reason is that the orientational effect accounted for in K_{or}^T is based only on the mutual orientation of the two segments, whereas the behavior of K_{ass} depends on the orientation of all segments of the chain.

Hence, the fraction of associated chains in the presence of flow will be larger for the mixture with T-polymers.

Finally, let us consider a mixture of A- and B-homopolymers where both hydrogen bonded ''linear'' and T-polymers can be formed. As before, the B-polymers have only one acceptor (donor) group at one of their ends, whereas the A-polymers carry two donor (acceptor) groups, one at the end (for formation of ''linear'' associated chains) and another somewhere near the middle (for formation of associated T-polymer). Of course, it is possible that both donor groups of the A-chain react, in which case a complex linear/T-polymer will be formed [Fig. 8(B)]. Similar to the analysis given above, from minimization of the free energy of the mixture the following equations for the association rates can be obtained [cf. Eqs. (31) and (40)]:

$$
\frac{\mathcal{N}_{AB}^L}{V} = K_o K_{ass} K_{or} \frac{(\mathcal{N}_A - \mathcal{N}_{AB}^L - \mathcal{N}_{AB}^T - \mathcal{N}_{AB}^*)}{V}
$$
$$
\times \frac{(\mathcal{N}_B - \mathcal{N}_{AB}^L - \mathcal{N}_{AB}^T - 2\mathcal{N}_{AB}^*)v}{V}, \tag{44}
$$

$$
\frac{\mathcal{N}_{AB}^T}{V} = K_o K_{or}^T \frac{(\mathcal{N}_A - \mathcal{N}_{AB}^L - \mathcal{N}_{AB}^T - \mathcal{N}_{AB}^*)}{V}
$$
$$
\times \frac{(\mathcal{N}_B - \mathcal{N}_{AB}^L - \mathcal{N}_{AB}^T - 2\mathcal{N}_{AB}^*)v}{V}, \tag{45}
$$

$$
\frac{\mathcal{N}_{AB}^*}{V} = K_o^2 K_{ass} K_{or} K_{or}^T \frac{(\mathcal{N}_A - \mathcal{N}_{AB}^L - \mathcal{N}_{AB}^T - \mathcal{N}_{AB}^*)v^2}{V}
$$
$$
\times \left(\frac{(\mathcal{N}_B - \mathcal{N}_{AB}^L - \mathcal{N}_{AB}^T - 2\mathcal{N}_{AB}^*)}{V} \right)^2, \tag{46}
$$

where $\mathcal{N}_{AB}^L$, $\mathcal{N}_{AB}^T$, and $\mathcal{N}_{AB}^*$ are the numbers of hydrogen bonded ''linear,'' T-polymers, and complex linear/T-associated polymers, respectively.

It follows from Eqs. (44)–(46) that the fraction of ''linear'' polymers, $X^L = \mathcal{N}_{AB}^L/\mathcal{N}_A$, is related to that of T-polymers, $X^T = \mathcal{N}_{AB}^T/\mathcal{N}_A$, via

$$
X^L = \frac{K_{ass} K_{or}}{K_{or}^T} X^T. \tag{47}
$$

The fraction of each type of associated polymers and the total fraction of associated chains $X = (\mathcal{N}_{AB}^L + \mathcal{N}_{AB}^T + \mathcal{N}_{AB}^*)/\mathcal{N}_A = (X^L + X^T + X^*)$ can be obtained by numerically solving the set of Eqs. (44)–(46). The dependence of the fractions of different types of hydrogen bonded chains on flow rate is presented in Fig. 10. In the absence of flow the fractions of ''linear'' and T-polymers are of course equal, and they are smaller than the fraction of complex linear/T-polymers under the conditions chosen. We consider the case of relatively weak association ($H = 2000$ K, $\Delta = \pi/4$) and strongly asymmetric composition ($N_A = 50$, $N_B = 5$, $\Phi = 0.2$): the number of acceptor groups on A-chains is related to the number of donor groups (B-chains) as 1:20. With increasing flow rate associated ''linear'' and complex linear/T-polymers start to experience extra stretching (compared to the two homopolymer chains) and tend to dissociate, relieving B-polymers. As a result the fraction of ''linear'' poly-
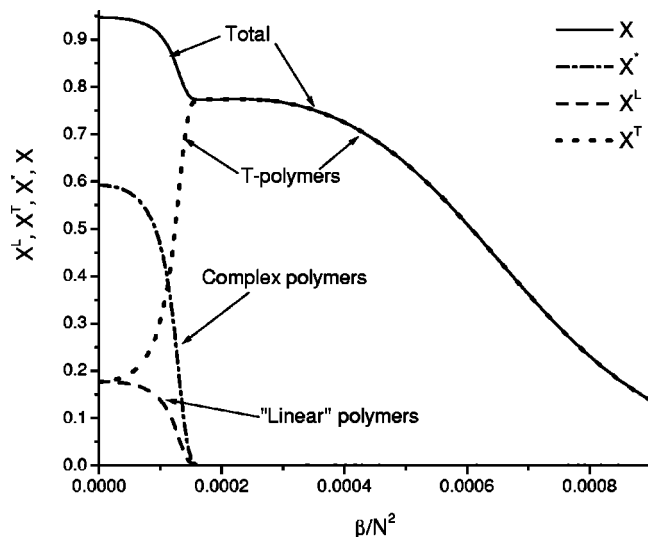
FIG. 10. Average fraction of associated ''linear'' polymers, X^L, T-polymers, X^T, complex linear/T-polymers, X^* and the total fraction of hydrogen bonded polymers, X, for the polymer mixture ($N_A = 50$, $N_B = 5$, $H = 2000$ K, $T = 400$ K, $\Delta = \pi/4$, $\Phi = 0.2$) vs flow rate.

mers X^L steeply decreases even though the orientation of the chains along the flow promotes hydrogen bonding, as discussed above. The fraction of complex linear/T-polymers also decreases quickly giving rise to T-polymers. For T-polymers the situation is different: there is no extra stretching of the hydrogen bonded chain and at weak flow rates the segment distribution is only slightly anisotropic, so that the probability to find main and side chains at nearly perpendicular orientation is still high. Moreover, the dissociation of complex linear/T-polymers increases the number of T-polymers as well as the number of free B-polymers (which also increases due to dissociation of the ''linear'' polymers). The relieved B-polymers can participate in the formation of T-polymers, which increases the fraction of T-polymers. Very quickly the fraction of T-polymers becomes dominant, while the fraction of complex linear/T-polymers and especially ''linear'' polymers becomes practically negligible. The total fraction of associated chains decreases only slightly confirming that at least half of the A-chains relieved by dissociation of ''linear'' polymers participates in the formation of T-polymers. At large flow rates, when all polymer chains tend to align along the flow direction, the penalty for nearly perpendicular orientation of segments next to donor and acceptor groups of hydrogen bonded T-polymers increases strongly, so that then the fraction of T-polymers, X_T, decreases together with the total fraction of associated chains, X.

There is a lack of experimental data concerning the behavior of hydrogen bonded blends under (elongational) flow, partially because of the general difficulty in counting the number of hydrogen bonds even for systems at equilibrium. Therefore we are not able to make a direct quantitative comparison of the predictions of our model with experimental data. However, we would like to draw attention to the recent experimental observations of unusual rheological behavior in two hydrogen bond involving polymer systems,[68,69] which

seems to be consistent with the predictions of our model. In the article,[68] [1]H nuclear magnetic resonance (NMR) spectroscopy experiments demonstrate a shear-dependent peak intensity for the glutamine amidic protons of wheat flour protein, (Amazonia) gluten, hydrated to 50% H_2O. The increase of the peak intensity under shear indicates the increase of mobility of the corresponding groups, which may be a result of hydrogen bonds disruption under shear.[68] After shear cessation the intensity of the peak diminishes to the original level. Similarly, the intensity changes in the NH_2 regions detected for the same polymer system subjected to extension are also consistent with the breaking and reformation of hydrogen bonds.[68]

The other polymer system is a semidilute solution of polyacrylamide (PAA) in water, also studied by (rheo-)NMR ^{1}H spectroscopy, which reveals an unusually slow relaxation after shear cessation.[68,69] Two relaxations processes, assigned to the restoration of shear-deformed reptation tubes (quick process) and hydrogen bonds reformation (slow process) have been distinguished. Thus, the origin of the slow relaxation can be in the formation of hydrogen bonds (disrupted by the shear) between neighboring amide groups. In addition, shear banding is observed in (relatively polydisperse) PAA solutions,[68,69] which is a characteristic feature of highly monodisperse systems (such as amphiphilic wormlike micelle solutions[16,20]). Shear banding can be associated with the breaking of a considerable fraction of hydrogen bonds in a high shear band, while in the slow shear band the fraction of hydrogen bonds is still large. This exactly matches the prediction of our model for elongational flow, that is, the fraction of hydrogen bonds under strong flow is much smaller than under the slow flow. Despite the fact that our model is expected to work properly only for elongational flow, the general trend of a decrease in the fraction of hydrogen bonds under increasing flow rate must hold for the shear flow as well, which will also elongate associated chains stimulating hydrogen bonds disruption.

IV. CONCLUSIONS

The association behavior of binary polymer blends was analyzed in the presence of an external elongational (flow) field. We were mainly interested in studying the steady state properties of one-functionalized polymers (below the entanglement limit) capable of forming single reversible orientationally dependent bonds (e.g., hydrogen bonds). The influence of flow was accounted for by considering (in the framework of a mean-field approach) the corresponding external potential acting on the polymer system. The effective free-energy approach has a limited applicability. It is valid only for polymer blends with relatively low fraction of long (associated or original) chains exposed to potential flows with $\gamma\tau \equiv \beta < 1$. The orientation distribution function for the dumbbell model of a polymer chain obtained by applying this approach reproduced the earlier result of Peterlin obtained by solving the diffusion equation. To obtain the orientation distribution function for the freely jointed model we generalized the approach assuming homogeneous extension of chains under flow and considering a mean potential acting on all segments of chains of equal length. It was shown that

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for a longer polymer chain or a stronger flow field the segment orientation along the flow direction increases.

The association constant K is strongly dependent on the flow rate through the product of two constants K_{ass} and K_{or}. K_{ass} describes the difference in stretching of the associated chain and the two initial homopolymer chains. Since longer chains are stronger stretched (and hence their segments more oriented), association into ''linear'' chains leads to a considerable additional entropy loss for associated polymers. As a result, the association constant K_{ass} rapidly decreases with increasing flow rate. The constant, K_{or}, describes the effect on association of the improvement of chain (segments) orientation. Since flow tends to orient the segments (chains) along the same direction, the probability to find a donor–acceptor pair at correct orientation for formation of ''linear'' diblock copolymer-like chains increases and hence K_{or}. However, K_{or} becomes appreciable only at relatively high flow rates, where K_{ass} is already rather small. Hence, a decrease of the association rate is predicted for ''linear'' associated polymers.

Next, the influence of chain architecture on the association constant under elongational flow field was considered. For mixtures of polymers of different length ($N_B \ll N_A$) capable of forming T-chains the association does not lead to extra stretching of the polymer chain ($K_{ass} \simeq 1$). Hence, the association constant K decreases purely due to the orientational effect (K_{or}^T), i.e., due to a decrease of the probability to find segments of the main chain and side chain at perpendicular orientation. The decrease in the association constant K for T-polymers is not as strong as that for ''linear'' polymers because there is no ''extra-stretching'' effect for T-polymers. As a result, in a mixture where both ''linear'' and T-polymers as well as complex linear/T-polymers can be formed, the relative fraction of T-polymers increases rapidly with increasing flow rate whereas the fraction of ''linear'' and complex linear/T-polymers strongly decreases. Very quickly the total fraction of associated chains is defined entirely by the fraction of T-polymers. At large flow rates the loss of orientational entropy becomes very large and T-polymers also dissociate into homopolymers.

Our prediction about the decrease of the fraction of hydrogen bonds (and associated chains) with increasing flow rate seems to be consistent with the recent experimental observations.[68,69] The unusual phenomena observed for polymer systems for which hydrogen bonding is involved are likely to be the result of hydrogen bonds rupture under flow and their reformation after flow cessation.[68,69]

ACKNOWLEDGMENTS

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