Dynamics of Hairy-Rod Polymer Solutions in Simple Shear Flow: Aging Effects

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ABSTRACT: We investigated the dynamics of solutions of a model hairy-rod polyester using optical rheometry and find that in the concentrated regime significant time effects dominate its response in simple shear flow. They are characterized by an enhanced viscosity and shear thinning behavior, accompanied by a corresponding increase of the absolute value of the induced birefringence and the relevant relaxation time upon cessation of shear. However, the most dramatic effect is the change of sign and large increase of the absolute value of the birefringence, signifying the dominance of form effects, associated with the formation of large anisotropic aggregates at longer times, which are oriented in the vorticity direction. This observation of anomalous birefringence is in qualitative agreement with the theoretical approach of Cates (*J. Phys. II* (*Fr.*) **1992**, *2*, 1109) who considered a presmectic local (anisotropic) ordering resulting from the interplay of particle interactions and the external field.

I. Introduction

The potential of rodlike polymers in solution to form liquid crystalline mesophases at high concentrations has opened the route for a systematic investigation of the interplay between structure and dynamics in such materials. It is now established that the isotropic−nematic transition is accompanied by a rich dynamics, characterized by the coupling of translational and rotational motions, the multiplicity of relaxation modes for the concentration and orientation fluctuations,[1,2] and a complex rheological behavior.[3−7] The latter represents an important issue because of its implication to processing of these materials in order to obtain ultrahigh modulus products, such as fibers or films for optoelectronics.

The efficient use of rheooptical techniques[8] has enabled the investigation of the effects of shear or extension in inducing anisotropy and orientation of rodlike polymers.[9−13] The systems typically investigated included rodlike systems such as xanthan gum,[11] collagen protein,[9,10] and poly(*n*-hexyl isocyanate);[2,13] all of them are quite polydisperse in size and exhibit a tendency to form aggregates in solution. The latter feature is of particular concern, as it could couple to the nematic transition and complicate the response to an external flow field. Although the effects of concentration have been considered,[14−16] the kinetics of association and the corresponding effects of time, i.e., aging, on the dynamics have received less attention.[16]

Using recently synthesized model hairy-rod polymers, namely poly(*p*-phenylenes) bearing aliphatic side chains,[17] we have explored their dynamics of association under equilibrium conditions using photon correlation spectroscopy.[15] These polymers possess a large inherent optical anisotropy due to the phenyl rings, and their conformation is that of wormlike chains;[18] they form aggregates in solution even at low concentrations due to side-chain crystallization,[15] and their dynamics at high concentrations is dominated by the cluster response, showing signs of pretransitional local ordering, i.e., orientational correlations.[16,19]

In this paper, we extend the above work by studying systematically the effects of time on the response of solutions of a model wormlike hairy-rod polyester to a simple shear field. We find that their behavior changes drastically with time due to association, and identify the formation of large aggregates with the change of sign of flow-induced birefringence. This observation is consistent with the theory of Cates,[19] who rationalized the experimental findings of change of sign of electric birefringence in polyelectrolyte solutions[20] by invoking the local presmectic ordering of anisotropic particles with main polarizability axis perpendicular to that of the constituent particles following the external (electric) applied field, in a certain concentration range, resulting from a steric strong local coupling between orientation and separation of neighboring pairs of particles.

II. Experimental Section

Materials. The synthesis and characterization of a series of hairy-rod polyesters, namely poly(*p*-terphenylene terephthalates), abbreviated as TPPE, is described in detail elsewhere.[21] The molecular structure of the TPPE bearing hexyl side chains, used in this work, is shown in Scheme 1. The number-average molecular weight is $M_n = 20\,420$, and the polydispersity is $M_w/M_n \approx 3.5$. The average contour length is $L_n = 74.8$ nm. These types of molecules are semiflexible, and their persistence length is typically $l = 20$ nm.[18,22] For the determination of the overlap concentration, c^*, light scattering measurements at different concentrations were carried out; the concentration dependence of the scattered intensity exhibited a maximum which was identified with $c^* \approx 0.07$ wt % The onset of the concentrated regime is marked by the concentration $c^{**} \sim b^{-1} L_e^{-2}$, with $b \approx 1.2$ nm the average diameter of the molecule and L_e the effective contour length defined as[2] $L_e = (2l^2[L_n/l - 1 + \exp(-L_n/l)])^{1/2} \approx 46$ nm, thus yielding $c^{**} \approx 2.5$ wt %. Four solutions were prepared in tetrachloroethane, a reported good solvent with high boiling

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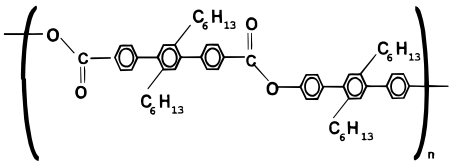
Scheme 1. Molecular Structure of Poly(*p*-terphenylene terephthalate) Molecules with Hexyl Side Chains (Hairs) Used



point (140 °C), to reduce evaporation problems, and density $\rho = 1.6$ g/mL, by adding the polymer to the solvent under strong stirring at 80 °C for 12 h: one in the semidilute regime (0.5 wt %), one in the semidilute-concentrated transition (2.7 wt %) and two in the concentrated regime (6.5% and 4 wt %). Whereas the first three solutions were only used for comparison purposes as fresh, the 4 wt % was investigated for an aging effect. The experimental protocol consisted of preparing a fresh 4% solution, loading it in the rheometer immediately after cessation of stirring, and leaving it there for 3 days. During this time consecutive rheooptical measurements were carried out (each day) and the aging results are reported and discussed below.

Methods: Mechanical and Optical Rheometry. Simultaneous measurements of viscoelastic and optical properties of the TPPE solutions were carried out by combining a Rheometric Scientific constant stress rheometer (DSR-200) with an optical train.[8,16,23] The latter includes a He−Ne laser generating a coherent polarized beam of power 5 mW at wavelength $\lambda = 632.8$ nm, which passes through the polarization state generator (PSG), the flow cell, and the polarization state analyzer (PSA). The PSG includes a polarizer, a photoelastic modulator (PEM) operating at a frequency of 50 kHz, and a quarter-wave plate, with respective orientations 0, 45, and 0° and net result a linearly polarized light (with orientation oscillating at 50 kHz and amplitude prescribed by the PEM) exiting the PSG. The flow cell consists of two parallel quartz plates of diameter 38.1 mm, with the sample loaded between them (the sample thickness was 1 mm). The PSA consists of a circular polarizer (CP) and a photodiode. When the CP is in the optical path, this configuration measures both birefringence ($\Delta n'$) and dichroism ($\Delta n''$); on the other hand, when it is removed, the measurement provides directly the dichroism. In this work, no dichroism signal could be detected beyond the instrumental resolution (about 10^{-9}), due to the small optical path through the sample. Thus, with the CP in place, the flow birefringence was measured. The Fourier expansion of the transmitted intensity in the photodiode is $I = I_{DC} + I_\omega \sin(\omega t) + I_{2\omega}\cos(2\omega t) + ...$, where I_{DC} is the DC component, $\omega = 50$ kHz is the frequency of the PEM, and the amplitudes of the first and second harmonics, I_ω and $I_{2\omega}$, respectively, are given for a sample with no dichroism by

$$I_\omega = I_{DC} R_\omega = -2 I_{DC} J_1 \cos 2\chi \sin \delta \quad (1)$$

$$I_{2\omega} = I_{DC} R_{2\omega} = 2 I_{DC} J_2 \sin 2\chi \sin \delta \quad (2)$$

with the parameters J_1 and J_2 being the calibration constants of the Fourier decomposition, determined experimentally, and the angle χ defining the orientation of the principal direction of the refractive index tensor in the plane orthogonal to the axis of light propagation, relative to the polarizer direction. In such a case, the orientation angle relative to the flow direction is $\theta = \chi - 45$. For the specific flow geometry used, this angle is 0 or 90° due to symmetry considerations.[8] The retardation δ relates to the birefringence $\Delta n'$ in the same plane through $\delta = 2\pi \Delta n' d/\lambda$, with d being the optical path length. Using the normalized intensities R_ω and $R_{2\omega}$, measured in two lock-in amplifiers (at ω and 2ω, respectively), and with sampling times varying between 50 and 500 ms, we can calculate directly δ and χ from eqs 1 and 2.

Rheological measurements included step and steady rate sweep tests, which were carried out with the controlled strain option, in the shear rate range 1−600 s^{-1}. The temperature was maintained at 20 °C using the original DSR recirculating fluids bath, appropriately modified in order to fit in the optical train.[16]

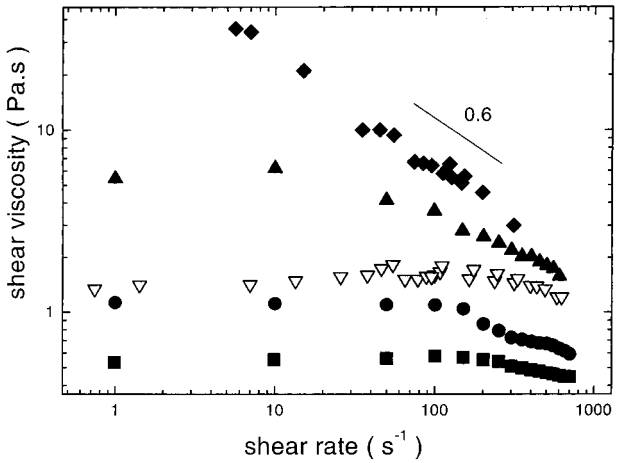


Figure 1. Steady shear viscosities of TPPE samples: 4 wt % (fresh, ■; 1 day old, ●; 2 days old, ▲; 3 days old, ◆) and 6.5 wt % fresh (▽).

III. Results and Discussion

Figure 1 depicts the steady shear viscosities for the 4 wt % TPPE solution in the fresh state and well as at later times, namely 1, 2, and 3 days after preparation. It is evident that time influences the dynamics of this solution a great deal, apparently through association characterized by a rather slow kinetics.[15] It is interesting that the fresh solution is nearly Newtonian exhibiting a weak shear thinning above 200 s^{-1} (with slope 0.2), whereas on the other hand the 1-, 2-, and 3-day old samples exhibit a clearly non-Newtonian behavior with shear thinning regions characterized by slopes 0.3, 0.4, and 0.65, respectively. Furthermore, for the 3-day measurement no Newtonian plateau was reached at the low shear rates; the strong thinning of the aged sample suggests supramolecular behavior, consistent with the time aggregation picture.[15,16] It is noted that at the end of the experiment (third day) and despite the precautions taken using a saturated atmosphere of solvent (with the aid of a solvent trap system) and the high boiling point of the latter, a small part of the sample evaporated. On the basis of the change of gap thickness in the parallel plates, we estimated that the maximum increase of the concentration with time due to evaporation did not exceed 50%, yielding a safely overestimated concentration of less than 6 wt %.[24] Nevertheless, the observed effects are dominated by the kinetics of association with time rather than the increase of concentration, thus we can still consider the aging problem unambiguously. To demonstrate this point, we present in Figure 1 the steady shear viscosity of a fresh 6.5 wt % solution. Thus, if we compare two solutions of the same concentration, one fresh and the other aged, the latter one is much more viscoelastic; this is an important result which clearly demonstrates beyond any doubt that the influence of time represents the cause of the non-Newtonian behavior through strong association.[16,25] This argument is supported by dynamic light scattering studies which clearly demonstrate the aging-induced aggregation in concentrated solutions of hairy-rod polymers.[15,25] Additional important evidence comes from the magnitude of the measured birefringence as discussed below.

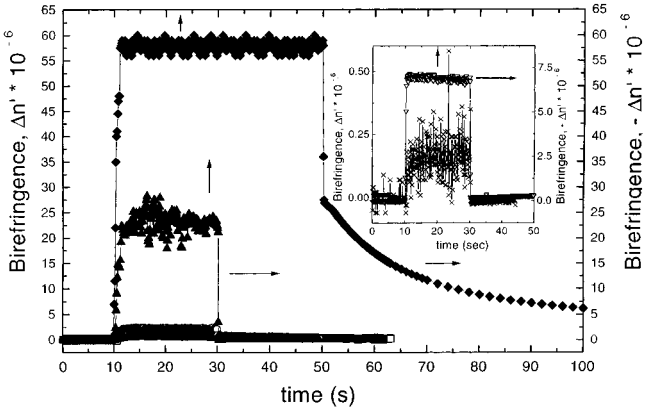


Figure 2. Transient birefringence $\Delta n'$ of various TPPE solutions in tetrachloroethane: 4 wt % fresh (■); 1 day old (○); 2 days old (▲); 3 days old (◆). Inset: 2.7% fresh (×); 6.5 wt % fresh (▽). All data are taken at $\dot{\gamma} = 200\ s^{-1}$.

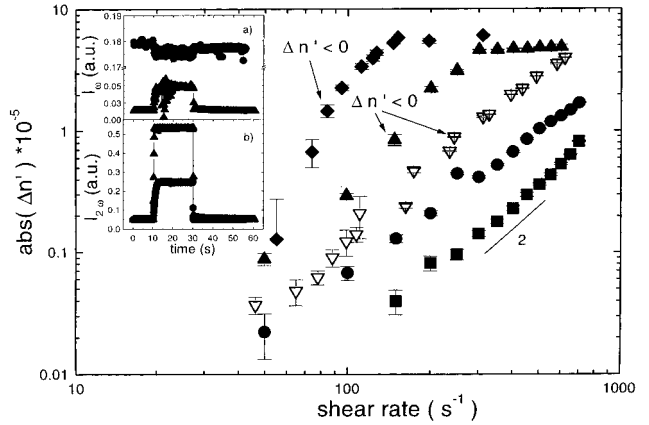


Figure 3. Steady-state birefringence (absolute values) as a function of shear rate for TPPE samples: 4 wt % (fresh, ■; 1 day old, ●; 2 days old, ▲; 3 days old, ◆); and 6.5 wt % fresh (▽). Inset: I_ω (a) and $I_{2\omega}$ (b) signals for a 1-day old sample (●) and a 2-day old sample (▲), respectively.

The birefringence induced by a simple shear flow was measured at different rates during step-up and relaxation experiments. Typical results are shown in Figure 2 for the examined aging sample at a shear rate of 200 s^{-1}; it is noted that no $\Delta n'$ signal could be resolved below 40 s^{-1}. For comparison the fresh 6.5 wt % solution is included in the inset of this figure, along with a fresh less concentrated (2.7 wt %) one; the latter is the lowest concentration above which the birefringence signal could be resolved. In this respect it should be pointed out that an even more dilute solution was measured for comparison (0.5 wt %), and besides the nonresolved optical signal, it was found that its rheological properties were virtually unchanged over the course of 8 days. It is interesting to observe in this Figure 2 that on day 1 and for the fresh 2.7 wt % solutions (inset) the induced birefringence is positive. On the basis of the structure of the TPPE molecule (Scheme 1), we know that its intrinsic birefringence is positive.[16] The quantities actually measured directly in the rheooptical experiment, i.e., the signals I_ω and $I_{2\omega}$, which relate to $-\Delta n' \cos 2\chi$ and $\Delta n' \sin 2\chi$, respectively (from eqs 1 and 2), are of opposite sign ($I_\omega < 0$ and $I_{2\omega} > 0$) for the 1-day old sample (inset, Figure 3), and of the same sign for the 2-day old sample (inset, Figure 3).[26] On the basis of these considerations, we suggest that at this low concentration we detect the (positive) intrinsic birefringence of TPPE molecules aligned in the flow direction ($\theta = 0°$).

On the other hand, for the fresh 6.5 wt % and 2- and 3-day old 4 wt % solutions, the sign of birefringence is reversed.[27] The fact that the birefringence sign changes from positive to negative with time, while its orientation angle now lies in the vorticity direction, was unambiguously deduced from inspection of both the I_ω and $I_{2\omega}$ signals, as illustrated in the inset of Figure 3. Actually, based on eqs 1 and 2 and the fact that the experimentally probed angle χ is considered with respect to the polarizer, it can be concluded that when I_ω and $I_{2\omega}$ have opposite signs, the detected birefringence is positive, whereas when they have the same sign, the birefringence is negative. This actually demonstrates the unambiguous detection of the sign of birefringence in the parallel plate geometry by taking advantage of both I_ω and $I_{2\omega}$ signals[16,28] (actually I_ω should be zero for perfect alignment in the flow direction, but experimentally in the present setup, it is not possible to align the polarizer at exactly 45° with respect to the flow direction during calibration). Therefore, in the case of the aged solutions we have $\Delta n' < 0$ and $\theta = -90°$. This result suggests, with the help of the simultaneous rheological information, that the origin of the measured flow birefringence relates to the presence of aggregates,[28] which in this case are formed with time at a fixed concentration and are of anisotropic shape.[8,16,28] Such changes of sign in the measured birefringence or dichroism have been reported in the literature and attributed to flow-induced rearrangements of colloidal aggregates[28] or relaxation of macromolecules through gel networks[29] or a change of fluctuations-induced dichroism orientation angle.[23] In the case of the aged solution (third day) the relaxation behavior is particularly remarkable as it shows a dominant very slow relaxation, in sharp contrast to all other cases, as discussed below. It is also noted, that in analogy to the viscosity data, the optical (and thus structural) response of the fresh 6.5% solution is clearly distinguished from that of the aged 4% ones. Furthermore, the fact that both aged 4% and fresh 6.5% solutions exhibit $\Delta n'$ sign reversal compared to the dilute solutions suggests an equivalence of time and concentration effects and the fact that in both cases a certain threshold cluster size has been reached giving rise to negative birefringence[11,16,19] (it is noted that it is impossible to molecularly disperse these hairy-rod polymers, even at low concentrations[15,16]); on the other hand, the difference in magnitude as discussed below, clearly indicates structural/size differences between the two solutions.

The extracted steady-state birefringence (absolute) values are plotted against shear rate in Figure 3. It is observed that within the experimental uncertainty the fresh samples and 1-day old 4% one follows essentially the scaling $|\Delta n'| \sim \dot{\gamma}^2$, whereas the 2- and 3-day old samples exhibit a stronger dependence with slopes of nearly 3 and 4, respectively. Moreover, with the exception of the fresh 4% sample, there is a decrease of slope as the shear rate increases and an eventual saturation of anisotropy is clearly observed for the more aged samples. Such a high-rate plateau was also observed in electric and flow birefringence experiments with a variety of wormlike polymeric systems[16,23,30] and was attributed again to saturation of birefringence at high values of the imposed field. It is also important to note that the magnitude of the birefringence of the 3-day old

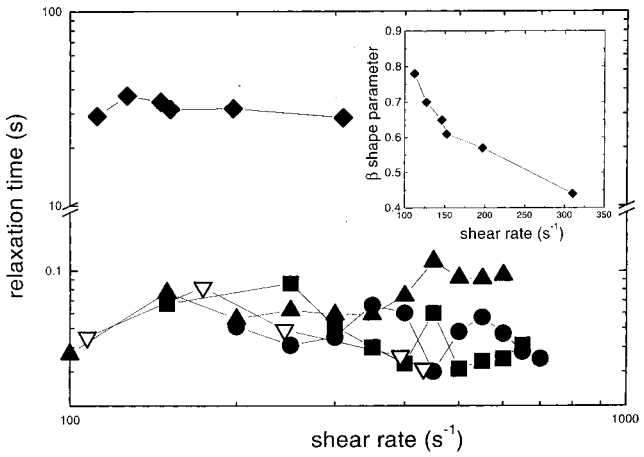


Figure 4. Extracted flow birefringence relaxation times for TPPE 4 wt % (fresh, ■; 1 day old, ●; 2 days old, ▲; 3 days old, ◆) and 6.5 wt % fresh (▽). Inset: Shear rate dependence of the respective extracted shape parameter for the 3-day old sample.

4% sample is much higher compared to the fresh 6.5% solution, and depending on the shear rate, it can exceed it by as much as 1.5 decades. Given the measurement conditions for the birefringence signal (the light beam crosses the sample at a radial position far from the edge,[16] of about $0.7R$, R being the radius of the plate), these data are much less influenced by the observed slight evaporation (as this effect is certainly more pronounced in the outer effect than in the inner of the sample); therefore, the birefringence data of Figure 3 reflect unambiguously the dominant effect of aging in cluster formation (without excluding a minor contribution from the limited evaporation).

The analysis of the birefringence relaxation upon cessation of the simple shear flow reveals interesting results which corroborate the time aggregation picture evolving. As clearly seen in Figure 4, for all cases except the 3-day old 4 wt % TPPE, one relaxation time (τ) is resolved, according to $\Delta n'(t) = \Delta n'_0 \exp(-t/\tau)^{\beta}$, where $\Delta n'_0$ is the amplitude of birefringence and β the shape parameter, being nearly 1. This time is virtually independent of shear rate (with an apparent increase during the second day at high shear rates), and changes weakly with time, within the experimental uncertainties (it varies from about 0.04 s for the fresh samples to about 0.1 s for the 2-day old sample at high shear rates). It is further noted that for the 2-day old sample β was smaller at high shear rates and reached a value of 0.8, indicating the possibility of additional relaxation; however, even in this case it was not possible to resolve two modes unambiguously. On the other hand, the 3-day old TPPE exhibits an initial ultrafast decay (Figure 2), which is faster than the time resolution of this experiment and probably relates to trimer species (the primary aggregate unit[16]) and clearly a broad dominant relaxation associated with the aggregates; the latter becomes broader as the imposed shear rate is increased (inset of Figure 4), suggesting that time is the main reason for association and that shear essentially deforms and breaks the clusters. For values of the shape parameter $\beta \leq 0.65$ ($\dot{\gamma} \geq 150$ s^{-1}) it is possible to fit the relaxation process with two single exponentials having times about 1 decade apart; however for the present purposes it is not useful to do so as the main result is a broad distribution of (deformed) cluster sizes. As seen in Figure 4, all times are virtually shear rate-independent, suggesting that the shear-induced breakup process is not dominant, and further that the aged sample contains larger entities (clusters) compared to the samples up to day 2; a weak increase of time a higher shear rates ($\dot{\gamma} > 400$ s^{-1}), suggesting a small growth of size (and consistent with a slightly reduced shear thinning in Figure 1) is observed for a day 2 sample. Compared to the respective behavior of fresh concentrated solutions,[16] the results of Figures 3 and 4 demonstrate that time is very important in affecting the association dynamics of these complex macromolecules,[15] and it should be properly accounted for before conclusions about their behavior at different concentrations are drawn. The fact that in the third day τ increased by more than 2 decades (Figure 4) signifies the formation of associations and corroborates the notion of rather slow kinetics of association in such wormlike chains, which is characterized by a sudden increase of size, probably related to overcoming an activation barrier $\Delta F_{act} \sim X$ where X is the major dimension of the anisotropic associating species.[15,31] The value of the cluster relaxation time in day 3 are similar to those reported by Gatzonis et al.[12] for aggregates from concentrated solutions of poly(*n*-hexyl isocyanate); in their case, the time difference between fast and slow relaxations extended up to 6 decades, but no change of sign was reported.

The extracted times of Figure 4 can be further rationalized as follows: The typical birefringence relaxation time upon flow cessation is $\tau = 1/6D_R$ where the simplest expression for the rotational diffusion coefficient is $D_R = (3k_BT)/(4\pi\eta_s R^3)$ with k_B the Boltzmann constant, η_s the solvent viscosity, and R the typical size of the cluster (here the latter is considered spherical, an assumption[15,16] which is not unreasonable for order of magnitude estimates). On the basis of the experimental results, the sample at day 3 consists of large clusters of typical size $R \approx 5$ μm, whereas the sample at day 2 has smaller clusters $R \approx 0.7$ μm and finally the fresh samples an even smaller $R \approx 0.4$ μm; the latter values are justified from dynamic light scattering measurements in poly(*p*-phenylene) systems.[25,15,16] It is interesting to note that a small change in the cluster size (from fresh sample to day 2 sample) corresponds to an inversion of the sign of birefringence; this suggests a possible path for trimer association into clusters (illustrated in Figure 5 below) via lateral interactions manifested as side chain (hairs) crystallization, in analogy to equilibrium studies,[15] and the presence of critical size for formation of anisotropic clusters at long times.[15,16,25]

Alternatively, the change of sign of birefringence should relate to large anisotropic entities, here above 0.5 μm.[32] On the other hand, given the molecular dimensions discussed in the experimental part above, a primary trimer unit which can be described roughly as a rod with[2,33] $D_{R,0} = (3k_BT)/(\pi\eta_s L_e^3)\ln(L_e/b)$ in the dilute regime would have an effective relaxation time of about 2.5 μs, which cannot be resolved with the present rheooptical technique; even if a concentrated trimer solution is considered, with $D_R = D_{R,0}(\nu L^3)^{-2}\beta$ to a first approximation (with $\beta \approx 10^3$ being the maximum crowding of the trimers[18] and ν the number concentration), the relaxation time (for 4 wt %) is about 80 μs. Therefore, the trimer relaxation was not detected.

The emerging picture from the above analysis is depicted in the cartoon of Figure 5. Whereas in the dilute regime $c < c^*$ (not considered here) the TPPE

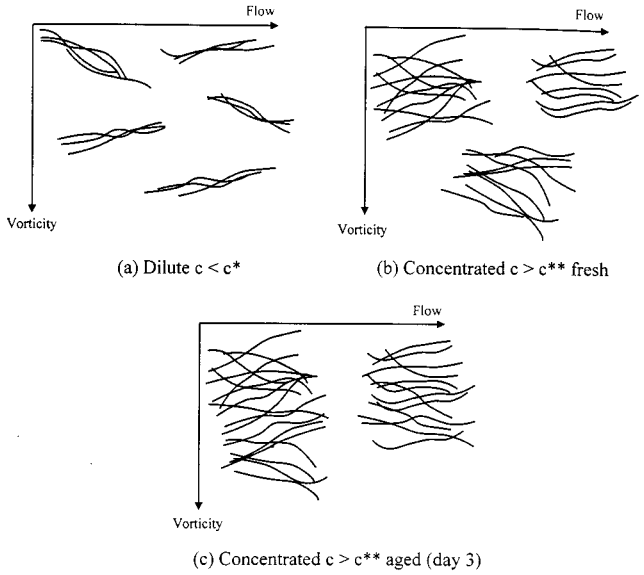


Figure 5. Schematic representation of the different states of sheared TPPE solutions in tetrachloroethane: (a) dilute $c < c^*$ consisting primarily of trimers; (b) concentrated $c > c^{**}$ (4 wt %) fresh consisting of smaller clusters; (c) concentrated $c > c^{**}$ (4 wt %) aged (3 days old) consisting of larger anisotropic clusters.

'molecular' species consist of trimers which can orient in the flow direction[15,16] (Figure 5a), the (fresh) concentrated regime $c \geq c^{**}$ is characterized by larger associations with positive birefringence, which also orient in the flow direction (Figure 5b). However, as time elapses much larger anisotropic clusters are formed with their main axis along the vorticity direction but with internal anisotropy along the flow (Figure 5c). Concerning the latter, the information from both birefringence magnitude (Figure 3) and relaxation times (Figure 4) suggests that the proposed structures correspond to steady-state behavior for the shear rate range investigated. This picture which can rationalize the experimental findings is also consistent with the theoretical considerations of Cates,[19] who predicted such an anomalous sign of (electric) birefringence in presmectic clusters of polyelectrolytes, as a result of a strong local coupling between flow orientation and steric interactions of neighboring pairs of particles, which eventually yields local order with cluster polarizability perpendicular to that of the constituent particles following the external (electric) field. In this language, the combination of effective steric interactions of the trimers or smaller clusters and the flow field (though imposed orientation at local scale) should be responsible for this observed change of sign in the birefringence response. As this birefringence anomaly depends on the orientation of the clusters, the birefringence signal should saturate very easily at high rates, in harmony with the experimental results of Figure 3. Finally, it is conceivable that at very high shear rates we should expect disruption of this type of ordering (via cluster breakup) and again change of the birefringence sign, but we have not seen this in our experiments in the examined shear rate range.

IV. Conclusions

We investigated the effects of aging on the dynamics of wormlike polyester solutions in simple shear flow with optical rheometry. We found that in the concentrated regime (above the estimated c^{**}) significant time effects, reflecting cluster formation, dominate the response of this polymer. They are characterized by an increase of viscosity and enhanced shear thinning behavior, as well as an increase of the absolute value of the induced birefringence and its relaxation time upon cessation of shear. More interestingly, the change of sign of birefringence found in aged solutions, along with the large increase of magnitude, signifies the dominance of form effects associated with aggregation (as opposed to fresh solutions of the same concentration) into large anisotropic clusters oriented along the vorticity direction. It is emphasized that whereas some unavoidable slight evaporation of the solvent (despite all precautions taken) is also a contributing factor, the dominant effects leading to the aggregate formation relate clearly to the aging of the solutions, as unambiguously demonstrated by the combination of rheological and optical experimental evidence and the agreement with relevant light scattering studies. Such an anomalous behavior can be rationalized by considering the flow-induced local ordering of sterically interacting species.

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(24) In the first 2 days the rheometer gap was virtually unchanged. It is further noted that all results were entirely reproducible. It is also noted that the third-day measurements were carried out with the properly adjusted gap, and the viscosity data are reliable and exclude the possibility of erroneous contribution due to potential formation of a "thin crust" of solution near the sample edge or other relevant pitfalls.
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(26) Note that for the estimation of the sign we consider the increase (($I_\omega > 0$ or $I_{2\omega} > 0$) or decrease of the signal with respect to the baseline; see also the inset of Figure 3 and ref 27 below).
(27) It is noted that all fresh solutions with $c < 5$ wt % exhibited positive birefringence, whereas fresh solutions with $c > 5$ wt % exhibited negative birefringence.[25]
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(31) This argument is consistent with the proposed association picture of Figure 5, where clusters are formed via lateral interaction (through the side chains) of trimers and/or smaller clusters.
(32) On the other hand, the presence of a small number of larger clusters at day 2, with relaxation times comparable to day 3, cannot be excluded; in such a case, however, their limited number inhibits their resolution based on intensity ($\Delta n'$) considerations.
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