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Shear Flow of Liquid-Crystalline Polymer Solutions As Investigated by Small-Angle Light-Scattering Techniques

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ABSTRACT: The shear flow of liquid-crystalline solutions of (hydroxypropyl)cellulose in water and poly(γ-benzyl L-glutamate) in *m*-cresol has been investigated by small-angle light-scattering techniques. A comparison between the rheological and rheooptical properties shows that the physical mechanisms involved under the shear flow undergo a drastic modification at the onset of the shear thinning region at high shear rates. A new structural model, based on the defects concept, is proposed for the rheology of lyotropic polymers.

Introduction

The rheology of main-chain polymeric liquid crystals is well documented as reviewed by Wissbrun.[1] Their flow behavior is rather complex and characterized by several unusual phenomena as compared to isotropic polymers. Among these rheological peculiarities are the occurrence of a negative normal force,[2-5] a low die-swell,[6-9] a shear thinning region at low shear rates,[5,10,11] and shear-induced textures.[5,12-16] However, the physical mechanisms responsible for such peculiar rheological behaviors are far from being well understood. A large number of papers[1,10,17-23] referred to "domains" for lyotropic and thermotropic liquid-crystalline polymers that might be responsible for their complex rheology. The domain concept suggested by Onogi and Asada[10] to describe the flow behavior of lyotropic nematic, or cholesteric, polymers leads to a three-region flow curve, which is commonly used as a reference. These authors proposed that at rest the polymer is composed of a "piled polydomain structure", a domain being a piece of space with a common director. At very low shear rates, the domains flow but keep their integrity. At an intermediate shear rate, some domains coalesce into a continuous phase where the director is everywhere the same and is supposed to be oriented along the flow direction. At high shear rates a continuous monodomain structure is achieved. Subsequently, Marrucci[24] and Wissbrun[25] have incorporated this concept into rheological models, which can predict some qualitative features of the experimental observations. However, it must be noticed that these theoretical predictions are mainly compared to viscosity measurements, which alone cannot elucidate the contribution of the "polydomain" structure to the rheology. The only proven fact is that polymeric liquid crystals form complicated superstructures or textures, which obviously strongly affect their flow properties. To understand the physical mechanisms involved under the flow of these supermolecular structures, it is now well established that rheooptical techniques are absolutely necessary. For this reason we used a flow-SALS (small-angle light-scattering) technique to measure the rheooptical properties of two different lyotropic polymers under shear flow. To complete our investigations, we compared these optical measurements with the rheological properties in order to classify the contributions of the structure to the rheology of the lyotropic polymers. A qualitative model[15] involving the notion of defects will be developed. Only two regimes, or regions, can be seen in the rheology of mesomorphic polymer solutions, instead of three as in the Onogi-Asada model.

Experimental Section

Material. The experiments were performed with two polymer solutions. The first was a 60 wt % solution of (hydroxypropyl)cellulose (HPC) Klucel E (M_w = 60 000), kindly supplied by Hercules. It was prepared by mixing water with HPC at room temperature followed by centrifugation to remove air bubbles. The second consisted of poly(γ-benzyl L-glutamate) (PBLG) at 19.3 wt % in *m*-cresol. The weight average molecular weight was 3.07×10^5. Both solutions were completely anisotropic at rest and developed a cholesteric structure.

Rheooptical Measurements. The optical measurements on the PBLG-*m*-cresol 19.3 wt % solution were carried out at the Kyoto University using a modified cone-and-plate rheometer (IR-200 Iwamoto Seisakusko Co., Ltd., Kyoto, Japan) and a 633-nm-wavelength laser described in ref 16. Similar measurements were performed on the 60 wt % HPC E solution at the Ecole Nationale Supérieure des Mines de Paris on a transparent Instron 3250 cone-and-plate rheometer described in ref 15.

The flows of these two solutions were followed by V_H (or H_V), V_V, and H_H light scattering. The first letter specifies the position of the analyzer, V meaning that the analyzer is parallel to the flow direction.

Results and Discussion

The supermolecular structures that occur under the steady-state shear flow have been extensively studied by V_H, V_V, and H_H scattering. A complete interpretation of all these scattering patterns is in preparation and will be discussed later.[26] For our purpose, only the V_H patterns (or H_V, which gave the same results), which are the most relevant for the comparison with the rheological flow curves η versus $\dot{\gamma}$, are presented here.

Figures 1 and 2 show the steady-state shear viscosity as a function of shear rate and the corresponding H_V scattering patterns for the PBLG-*m*-cresol solution and V_H scattering patterns for the HPC-water solution. The most prominent feature is that for both solutions the flow-induced structures undergo a continuous modification beginning from a slight deformation below a certain critical shear rate $\dot{\gamma}_c$ up to a fully complex SALS pattern above $\dot{\gamma}_c$. Below this critical shear rate the SALS patterns are

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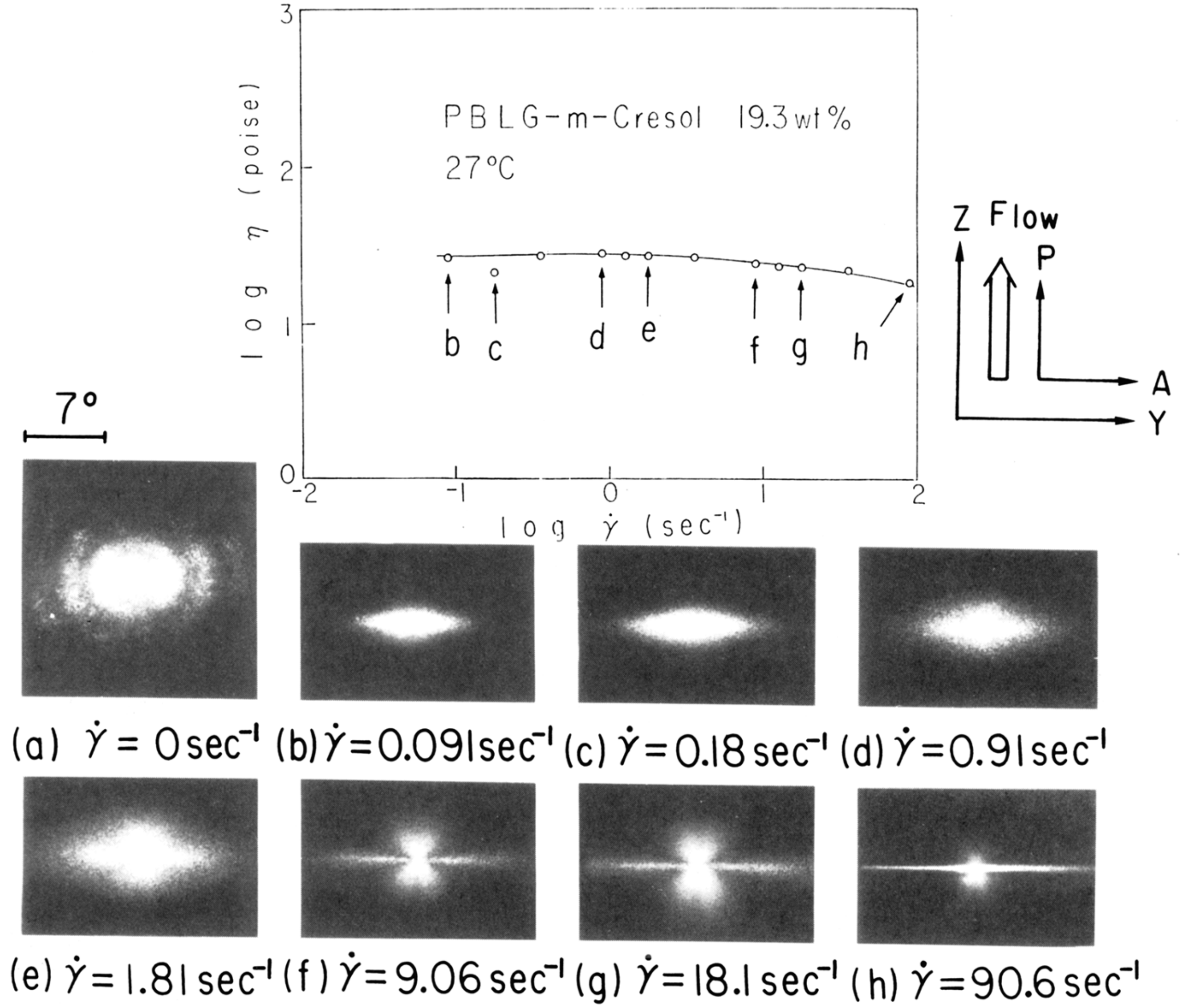


(a) $\dot{\gamma}$ = 0 sec^{-1} (b) $\dot{\gamma}$=0.091 sec^{-1} (c) $\dot{\gamma}$=0.18 sec^{-1} (d) $\dot{\gamma}$=0.91 sec^{-1}

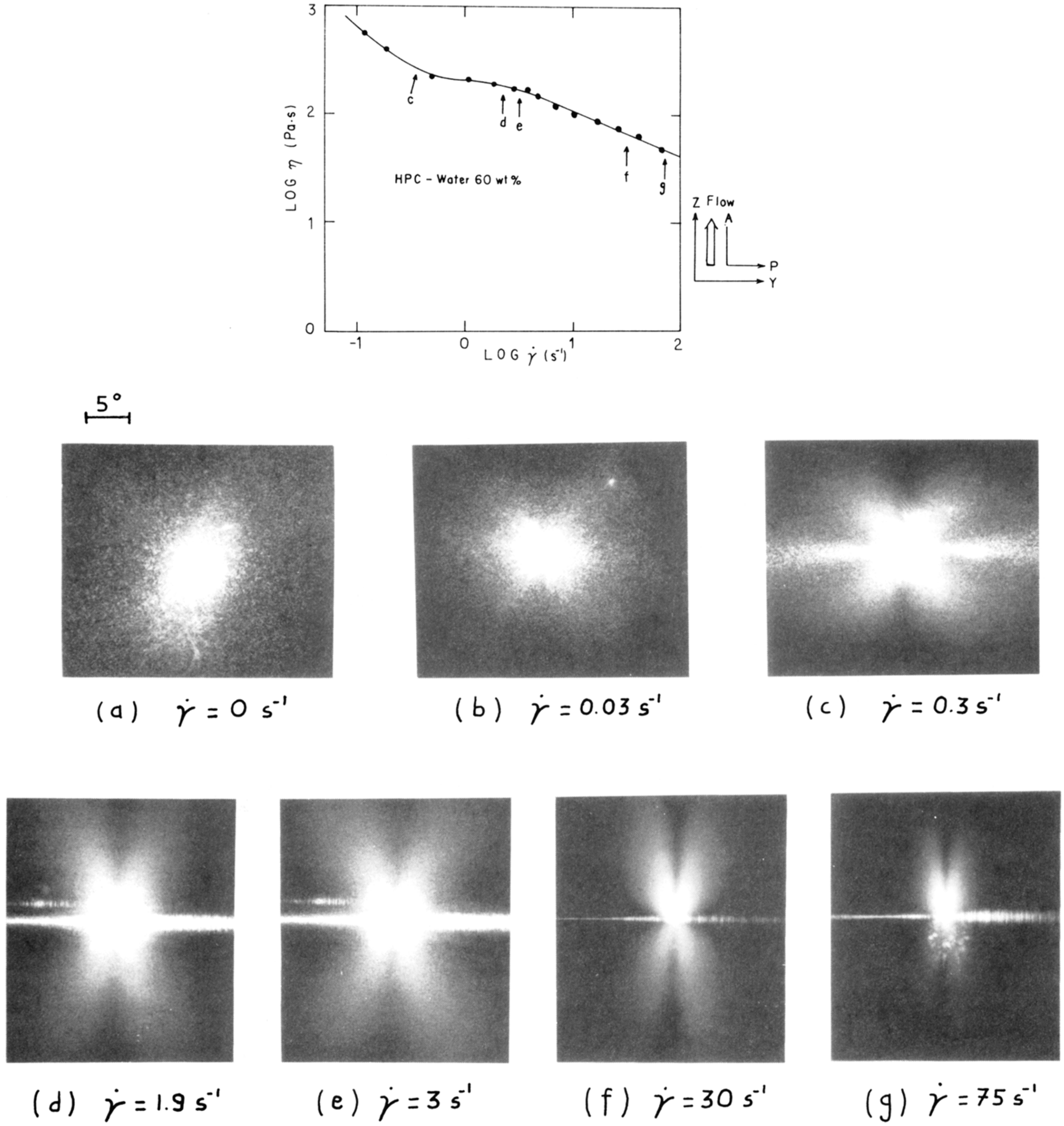
(e) $\dot{\gamma}$=1.81 sec^{-1} (f) $\dot{\gamma}$=9.06 sec^{-1} (g) $\dot{\gamma}$=18.1 sec^{-1} (h) $\dot{\gamma}$=90.6 sec^{-1}

Figure 1. Steady-state shear viscosity, η, and H_V scattering pattern as a function of shear rate, $\dot{\gamma}$, for the PBLG–*m*-cresol solution.

characterized by somewhat elliptical profiles with their long axis perpendicular to the flow direction. On the other hand, above this critical shear rate these elliptical patterns transform to an X-type profile as seen for oriented and deformed anisotropic rodlike superstructures[27–29] with an additional equatorial streak perpendicular to the shear flow. The transition described above occurs between approximately 0.3 and 2 s^{-1} for the HPC–water solution and between 1 and 4 s^{-1} for the PBLG–*m*-cresol solution: from Figures 1 and 2 it is clearly shown that the onset of the shear thinning at high shear rates is comprised between these shear rate ranges where the transition is observed.

As shown by the light-scattering profiles in Figures 1 and 2, the structural changes involved during the shear flow are characterized by only two regimes (or regions): a regime A at low shear rates where only a slight distortion of the quiescent pattern is observed and a regime B at high shear rates where the depolarized patterns have undergone characteristic changes. An interesting point is that, as seen by SALS, the behaviors of HPC and PBLG are the same, despite the fact that there are marked differences in polymer structure and rigidity and in the flow curves. Another feature is that the transition between the two types of SALS patterns occurs for both polymers at the onset of the last shear thinning region, when the shear begins to have an effect for orienting the individual molecules. These two facts suggest that only two regimes, or regions, exist in these solutions: a regime A, at low shear rates, where the shear does not orient the molecules enough to strongly modify the defect structure, and a regime B, at shear rates higher than the onset of the shear thinning region, where the orienting effect of the shear changes the structure. These structural changes have several effects on the SALS patterns and on the rheology (new relaxation mechanisms as the band pattern[5,12–15,26] or negative normal forces[2–5]). On the basis of the information available on the rheology and rheooptics of these two polymer solutions and on recent experiments concerning the behavior of defects in polymer liquid crystals, a qualitative picture of these two regimes is proposed.

Regime A. Low Shear Rate Regime $\dot{\gamma} \ll \dot{\gamma}_c$. In this shear rate range the rheooptical behavior is characterized by V_V and V_H (or H_V) patterns similar in shape and having nearly equal intensities, which means that the orientation correlations are governing the flow; i.e., density and concentration fluctuations are insignificant.[26] The role of the disclinations in the rheology has been emphasized by two of the authors.[30] To explain the unusual rheological behavior of cholesteric HPC–water solution, they suggest that defects (disclinations) form a network



(a) $\dot{\gamma} = 0$ s^{-1} (b) $\dot{\gamma} = 0.03$ s^{-1} (c) $\dot{\gamma} = 0.3$ s^{-1}

(d) $\dot{\gamma} = 1.9$ s^{-1} (e) $\dot{\gamma} = 3$ s^{-1} (f) $\dot{\gamma} = 30$ s^{-1} (g) $\dot{\gamma} = 75$ s^{-1}

Figure 2. Steady-state shear viscosity, η, and V_H scattering patterns as a function of shear rate, $\dot{\gamma}$, for the HPC–water solution.

extending through all the sample. Recently Shiwaku et al.[31] and Hudson et al.[32] have visualized disclinations in liquid-crystalline polymers using, respectively, light microscope and transmission electron microscope techniques. They observed that arrangements of disclinations could give a complex structure consisting of regions of uniform molecular orientation bounded by disclinations. Defects can be arranged in an ordered manner[32] or at random[31,33] depending on the nature of the texture. This gives a flow that has been largely described in the literature by the domain model. However a description of this flow with different physical pictures associated with the term domain, which may be independent and rigid, is inadequate. Such a model would probably give a yield stress, which does not exist in these solutions and will have a zero average orientation if the domains are tumbling or rolling, which is not the case as seen by SALS. Moreover, the nature of the boundaries (planar domain wall) between these domains is difficult to imagine in physical terms, both in quiescent state and in steady-state flow field.

Nevertheless, transient simple shear experiments on similar polymer solutions show a behavior that is analogous to that of a suspension,[34] due to the complex flow of the defects.

A proper description must include the motion of defects in the polymer solution, which is an unknown subject (even for small-molecule liquid crystals under a shear). However, we attempt to describe qualitatively the motion below.

We propose the following qualitative description based on the SALS and optical observations: at rest, defects (mainly disclination lines) are present in the polymer. The flow, at low shear (or strain) rate, cannot significantly orient the molecules and cannot force the defects to rearrange to a large extent. Their spatial position and orientation are essentially at random though slightly distorted. Flow will take place with these constraints. The average orientation is very weak and is due to regions where defects are far away. This gives rise to an ellipsoidal orientation correlation as implied by the scattering patterns shown in Figures 1 and 2, where the greater correlation distance is along the shear flow. What will cause this regime to change is not the disappearance of the defects (as in the region II → region III mechanism of the Onogi–Asada model) or the increase of their number (as in the Wissbrun model, where the domain size decreases with the shear rate) but more the different spatial arrangement seen by SALS, due to the orienting effect of the flow. This is the second regime, regime B.

Regime B. High Shear Rate Regime $\dot{\gamma} \gg \dot{\gamma}_c$. When the shear rate is larger than the critical shear rate, $\dot{\gamma}_c$, the viscosity is shear thinning and the SALS pattern is composed by a long streak and four lobes. In this shear rate range, the shear rate is larger than the inverse of the longest relaxation time, and the molecules will strongly feel the orienting effect of the flow. Despite the fact that there is a theoretical doubt[35] about the possibility for a nematic polymer to attain a stable orientation under shear, we will consider that, in this regime, the stationary configuration of the defects at the low shear rate regime is destroyed and part of the molecules will achieve a uniform orientation in the shear flow, the remaining defects being strongly distorted and localized. This remains an hypothesis as far as lyotropic polymers are concerned. It has nevertheless some grounds since it has been proven by optical microscopy[33,36] that the texture of main-chain thermotropic polymers is due to groupings of disclinations of opposite sign. Considering that this is the case with our two lyotropic polymers, we can imagine that during the flow at high shear rates the defects will be located in some areas. In other words the fluid can be divided in two regions as shown in Figure 3:[26] a region M, more or less uniform with a high average orientation order and very low density of defects, and regions D, highly concentrated in defects. The existence of these regions D is highly probable, as seen by the spatial polarizability fluctuations, which are significant at high shear rates.[26] Under all the polarization conditions, the scattered intensity decreases while increasing the shear rate. This suggests that the amount of the defect regions will decrease and that the sample will tend to achieve a monodomain at very high shear rates.

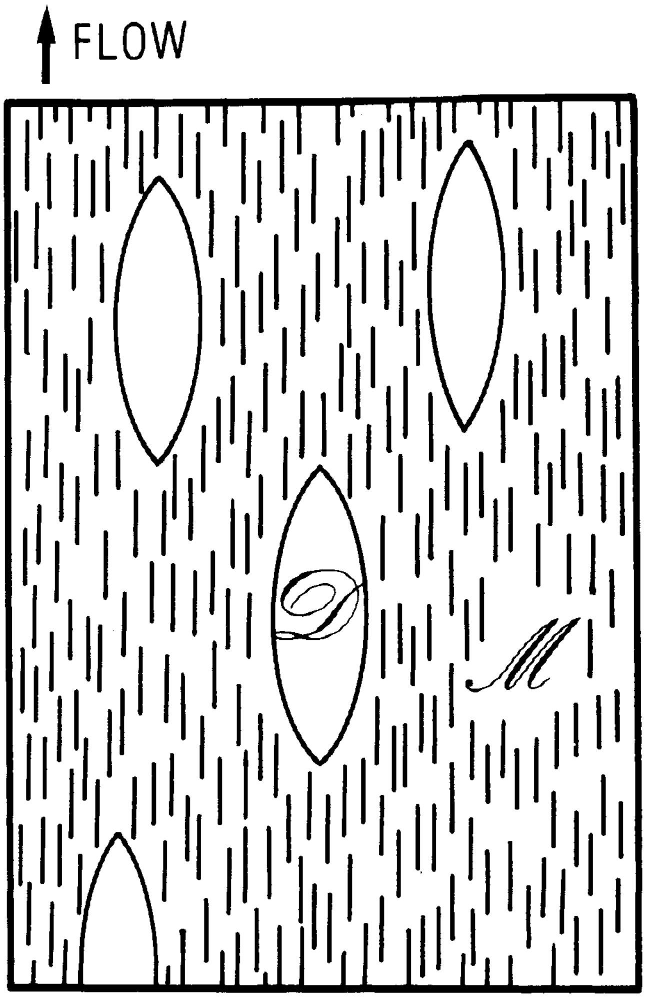


Figure 3. Model of the flow for $\dot{\gamma} > \dot{\gamma}_c$.

Conclusion

The SALS resuls show that the model suggested by Onogi and Asada,[10] which up to now was very convenient to describe the flow curve η vs $\dot{\gamma}$, does not fit the light-scattering experiments well. First, we find only two physical mechanisms over the wide shear rate range used to describe the flow behavior of our two lyotropic polymers rather than the three structural mechanisms proposed by these authors. Second, their proposal predicts that in the shear-thinning regime at high shear rates (region III in their terminology) the polymer solution should be transformed in a continuous monodomain. This is in contradiction with our optical observations,[15,16,26] which show that defects are still present in region III, up to high shear rates. Although there is a tendency toward the monodomain, the achievement of the monodomain at a very high shear rate is still difficult to experimentally assess. Finally, the notion of domains that could move, could be broken or deformed, and could be compared to polymers filled with solid spheres or short fibers[23,37-39] is probably an incorrect analogy. Spatial orientation correlations and constraints due to the presence of defects drive the flow and the relaxation.

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Registry No. HPC, 9004-64-2; PBLG (homopolymer), 25014-27-1; PBLG (SRU), 25038-53-3.

Synthesis and Characterization of Poly[[*o*-(trimethylsilyl)phenyl]acetylene][1]

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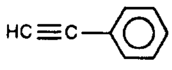
ABSTRACT: [*o*-(Trimethylsilyl)phenyl]acetylene quantitatively polymerized in the presence of WCl_6–Et_3SiH (1:1), $W(CO)_6$–$h\nu$, and $MoCl_5$–Et_3SiH (1:1) catalysts in toluene or CCl_4 at 30 °C to give a new polymer having weight-average molecular weight over 1×10^6. Effects of organometallic cocatalysts, solvents, and temperature on the polymerization were studied. The product polymer possessed the structure $[-CH{=}C(C_6H_4\text{-}o\text{-}SiMe_3)-]_n$ and was amorphous. The polymer was in the form of a dark purple solid (λ_{max} 542 nm), completely dissolved in common organic solvents such as toluene and $CHCl_3$, formed a strong film by solution casting, and did not lose weight below 280 °C in air, being fairly thermally stable.

Introduction

It has recently been found that not only phenylacetylene (PA) but also ortho-substituted PA's such as (*o*-methylphenyl)acetylene[2] (*o*-MePA) and [*o*-(trifluoromethyl)phenyl]acetylene[3] (*o*-CF_3PA) polymerize with W and Mo catalysts. Quite interestingly, poly[(*o*-methylphenyl)acetylene] [poly(*o*-MePA)] and poly[[*o*-(trifluoromethyl)phenyl]acetylene] [poly(*o*-CF_3PA)] obtained have higher molecular weights than that of poly(phenylacetylene) [poly(PA)] irrespective of the steric hindrance due to the ortho substituents. Eventually poly(*o*-CF_3PA) provides a strong film by solution casting, whereas poly(PA) is too brittle to form a free-standing film.

So far, a number of substituted polyacetylenes have been synthesized by using transition-metal catalysts.[4] Among those polymers are Si-containing polyacetylenes, some of which exhibit unique properties not seen in hydrocarbon polyacetylenes. For example, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] shows extremely high gas permeability[5] and ethanol permselectivity in the ethanol/water pervaporation.[6]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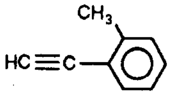
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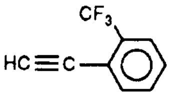
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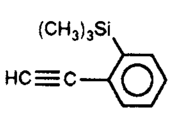
o-Me_3SiPA

[*o*-(Trimethylsilyl)phenyl]acetylene (*o*-Me_3SiPA) is an ortho-substituted PA and is a Si-containing acetylene as well. It is of interest to study the polymerizability of this monomer, the molecular weight of poly[[*o*-(trimethylsilyl)phenyl]acetylene] [poly(*o*-Me_3SiPA)], and properties of this novel polymer. In this paper we report on the polymerization of *o*-Me_3SiPA and on the characterization of poly(*o*-Me_3SiPA).

Results and Discussion

Polymerization by Various Catalysts. It has been found that mixtures of WCl_6 or $MoCl_5$ (main catalyst)

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