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# Worm-like morphology of semi-rigid substituted poly(*p*-phenylene)

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**Abstract** The rheological and dynamic mechanical properties of a semi-rigid substituted poly(*p*-phenylene) were investigated. At temperatures below the glass transition temperature of 152 °C the amorphous polymer is very stiff compared with flexible chain polymers. Although the material can be processed in the melt, the melt is unusually elastic. Atomic force and transmission electron microscopy revealed a worm-like morphology. Blends with polycarbonate yield transparent materials. Microscopy and X-ray diffraction of these blends indicated that the flexible chain polymer is located in between the worm-like structures of the semi-rigid polymer.

## Introduction

During the last three decades, research on rigid chain polymers, both in industry and academia, has been highly fruitful with regard to both fundamental science and material science [1]. Research workers have, however, not yet succeeded in developing materials with high temperature stability, low viscosity at high shear rates and superior homogeneous material properties.

The processing behavior and material properties of liquid crystalline polymers (LCPs) and flexible chain polymers with liquid crystalline side chains have been modified by incorporating non-crystalline, non-linear or flexible molecules between the mesogenic groups [1, 2]. The complicated morphological structures [3] yield highly interesting structure property relationships. Although there is a wide variety of LCPs with interesting properties and potential applications, only a few materials have gained commercial relevance. Some lyotropic LCPs have become very successful in the fiber industry in particular (e.g. poly(*p*-phenylene) terephthalamide/Kevlar® fiber).

Poly(*p*-phenylene) is well known for its high temperature stability, but unfortunately it is a highly crystalline polymer that is insoluble and infusible, and therefore cannot be processed by means of conventional processing techniques.

Marrocco et al. [4] have reported large-scale synthesis of processable high-molecular weight substituted polyphenylenes. Now several types of these processable semi-rigid polymers have been introduced under the trade name Parmax®. For an amorphous polymeric material, Parmax® has an unusually high Young's modulus of about 10 GPa and can be processed like a thermoplastic polymer. It is soluble in a few select organic solvents (e.g. methylene chloride, *N*-methyl pyrrolidinone, dimethyl acetamide), but not in common solvents such as toluene, alcohols, acetone, etc. A remarkable compatibility with several linear flexible polymers makes Parmax® a promising modifier and blend partner. Polyarylene can also be used as

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high-temperature, moisture-insensitive matrix resins in advanced composite materials [5] and self-reinforced foams [6].

In this paper, we report on the worm-like morphology of Parmax 1200® and its blends with bisphenol-A polycarbonate and the influence of this morphology on the rheological properties. The morphology was investigated by means of atomic force microscopy (AFM) and X-ray diffraction techniques.

## Experimental section

### Sample

The Parmax® 1200 sample was supplied by Mississippi Polymer Technologies, Inc. (MPT). Parmax® are polymers and copolymers based on poly(*para*-phenylene) structures that have substituents "R" derived from a variety of organic groups. In this paper we investigated Parmax® 1200—a copolymer based on benzoyl phenylene backbone modified with occasional non-para linkages (kinks) (see Fig. 1).

### Rheological investigations

The samples were compression-molded at 300 °C. The oscillatory shear measurements were performed using plate-plate geometry on a Rheometrics ARES rheometer. Plates with a diameter of 7 and 25 mm were used and the temperature range was between 180 and 300 °C with frequency sweeps from 0.01 to 10 Hz. The creep experiments were performed on a Paar-Physica UDS 200 rheometer at 300 °C. The onset of thermal degradation was determined by measuring the storage modulus as a function of the measurement time. These data were used to ensure that thermal degradation did not interfere with the rheological investigations.

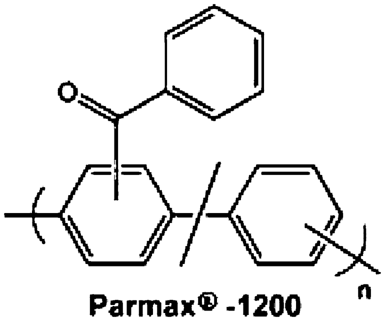

**Fig. 1** Chemical structure of Parmax 1200, a polyparaphenylene modified with occasional *m*-phenylene linkages (kinks)

### Dynamic mechanical analysis (DMA)

The DMA was also performed with the aid of a Rheometrics ARES rheometer. Compression-molded rectangular bars and circular sheets were used. A DMA temperature sweep from –150 °C up to about 200 °C was performed for the rectangular bars. Above the glass transition temperature of about 160 °C, the rectangular bars are no longer suitable and a plate–plate geometry, 7 mm in diameter, was used to make a second additional measurement at higher temperatures up to 300 °C.

### Atomic force microscopy (AFM)

The AFM measurements were performed with the aid of a commercial scanning force microscope (Digital Instruments D3000). The measurements were made in tapping mode with Si-tips (coated with a water absorption film) attached to 225 μm cantilevers, at resonance frequencies of about 60 kHz.

The X ray diffraction (XRD) measurements were performed on a commercial system (Bruker GADDS = General Area Detector Diffraction System). The polymer samples were measured as films. Reflection mode with Cu $K_\alpha$ radiation (0.154 nm) was used.

The Transmission Electron Microscopy (TEM) measurements were done on a Philips EM420 at 80 kV. The sample was microtomed at RT to a thickness of less than 0.1 μm and was stained with ruthenium tetroxide.

## Results and discussion

The reported [4] ultra-high stiffness of substituted poly(*p*-phenylene) was investigated by means of dynamic-mechanical analysis (DMA). The shear storage modulus of Parmax 1200 is about three times higher than that of polycarbonate, for example, at ambient temperature. Figure 2 shows the measurement of the shear moduli $G'$ and $G''$. At temperatures below the glass transition temperature, the measurements were performed on rectangular bars, at temperatures above the glass transition temperature parallel plate geometry was used. Connolly et al. [7] observed for substituted poly(*p*-phenylene) polymers only a very broad, weak secondary relaxation maximum between –100 and +50 °C, and concluded that the side groups had restricted mobility in the glassy state or that the local relaxation modes in the glassy state do not significantly dampen mechanical oscillations. They concluded that the temperature dependence of

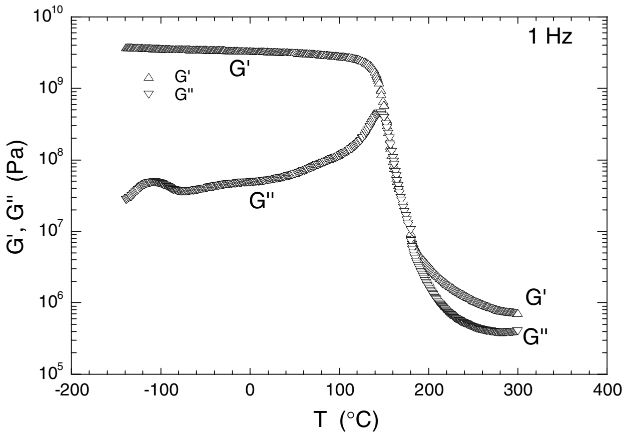

**Fig. 2** Storage and loss modulus of Parmax 1200 as a function of the temperature. The values below the glass transition temperature were determined on rectangular bars, the values at temperatures above the glass transition were determined using plate–plate geometry

dielectric and viscoelastic relaxation times in these substituted polyphenylenes can be explained by simple free volume considerations. The secondary relaxation at about $T = -110$ °C seen in Fig. 3 was not observed by Connolly et al. [7], probably due to the limited temperature range they used.

The thermal stability of the polymer was investigated very thoroughly in the present study Although TGA experiments showed that the onset of weight loss starts at about $T = 375$ °C and a rapid decrease in weight is not observed at temperatures below $T = 490$ °C, thermal degradation may start to change the rheological behavior at much lower temperatures.. Therefore the storage modules $G'$ measured as a function of time at a low frequency of $\omega = 0.06$ rad/s showed no increase up to measurement times of 1 h under nitrogen. At $T = 340$ °C an increase of about 30% in storage modulus was recorded in 1 h. Creep measurements performed at $T = 300$ °C showed a decrease in compliance at very long creep times ($t > 2.5$ h), probably due to thermal degradation. These thermal degradation data show that, for reliable rheological measurements, the temperature range should not exceed $T = 300$ °C and the measurement periods should be no longer than 2 h.

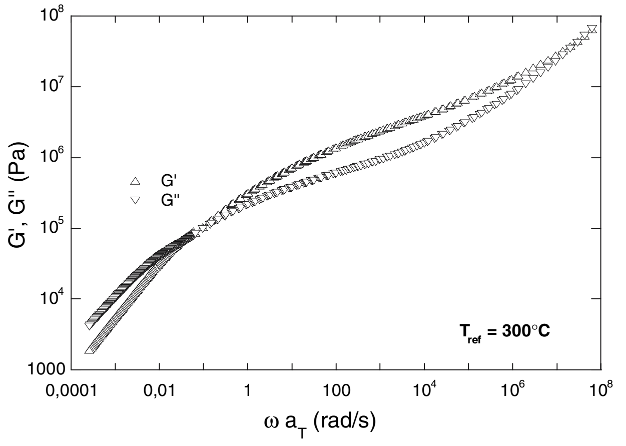

**Fig. 3** Master curves for the storage and loss modulus ($G'$ and $G''$) versus angular frequency from combined oscillatory shear and creep measurements at the reference temperature of $T = 300$ °C

As shown in Fig. 2, even at $T = 300$ °C and $f = 1$ Hz, the melt of Parmax 1200 is unusually elastic for a polymer. The rheological experiments performed in oscillatory shear at the lowest possible angular frequencies indicated that at even lower frequencies $G'$ and $G''$ might show a cross-over, i.e. the melt might change its character from elastic to viscous. Additional creep measurements were therefore performed at $T = 300$ °C with a maximum measurement time of $t = 1\ h$. The oscillatory data at a reference temperature of 300 °C were transformed into the compliance $J(t)$ by means of the non-linear regularization software NLREG [8]. These data points were combined with the compliance measured directly in creep measurements. From this combined data set, the master curve for the storage and loss modulus was recalculated with the NLREG software over a much larger frequency window (Fig. 3).

Although substituted poly($p$-phenylene) is thought to behave like a semi-rigid rod polymer, the rheological behavior shown in Fig. 3 resembles that of flexible chains with a broad molecular weight distribution. From these rheological results it is not surprising that Parmax can be extruded and that the viscosity can also be investigated in a high-pressure capillary rheometer, for example (Fig. 4). Again the viscosity at $T = 300$ °C is very high and shows the same shear thinning behavior as flexible polymer chains usually exhibit. In Fig. 4 the complex viscosity and the viscosity from capillary rheometry are shown as a function of the angular frequency and the shear rate. The data for the oscillatory shear measurements correspond relatively closely to the capillary rheometry measurements. Due to the flow-induced alignment of anisotropic polymers in the capillary rheometer, rigid rod polymers do not usually obey the Cox–Merz rule. At moderate shear rates, the data for oscillatory and capillary shear are still comparable; only at very high shear rates is the viscosity measured in capillary shear lower than that measured in oscillatory shear. These data show that Parmax behaves more like a flexible polymer than a semi-flexible polymer. As described by De Gennes [9], a nematic liquid crystalline material flows very much

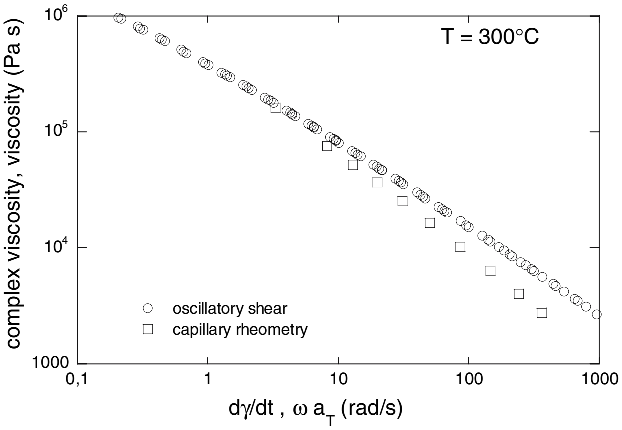

**Fig. 4** Viscosity measured in oscillatory shear and capillary rheometry as a function of the shear rate at 300 °C

like a conventional organic liquid with molecules of similar size, but the coupling between orientation and flow is much more complex.

Flexible chain polymers with different chemical compositions are known to be incompatible with each other unless an additional attractive force between the monomers of the blend components exist [10]. Parmax is known to be compatible with several flexible polymers, e.g. BPA polycarbonate. Blends of Parmax with polycarbonate are transparent, like their components Parmax and polycarbonate themselves. This does not mean that the blend is necessarily compatible on a molecular scale. The blend samples were therefore studied by means of atomic force microscopy to investigate the morphology of these blends on the nano-scale. Figure 5a shows the micrograph of the AFM phase contrast measurement on a microtomed piece of a compression-molded pure Parmax 1200 sample. Surprisingly, the substituted polyphenylene sample shows molecular aggregates. To make sure that this picture of the morphology is not an artifact, the structure is reproduced in transmission electron microscopy (TEM), as can be seen in Fig. 5b. Both in AFM and TEM the pure Parmax 1200 sample shows worm-like structures with a lateral dimension of about 0.1 μm, i.e. the diameter of such a worm like unit is about 220 times the diameter of one single polyphenylene molecule.

The worm-like structure resembles the morphology usually seen in co-polymers and blends due to spinodal decomposition [10]. Mississippi Polymer Technologies state that Parmax 1200 is bases on a benzoyl phenylene backbone modified with occasional non-para linkages [4–7], i.e. if this is true, the worm-like morphology is unlikely to be caused by spinodal decomposition.

The shown nano-scale morphology will probably also exist at higher temperatures and might be the explanation for the rheological behavior of the semi-rigid rod polymer investigated. Although the viscosity versus shear rate dependence in Fig. 4 resembles that of flexible chain polymers, the micro-rheology might be completely different.

Rheo-optical methods used to directly observe the morphology evolution during shear start-up and reversal flow in semi-flexible main-chain thermotropic liquid crystalline polymers [11] show a morphology totally different from the morphologies shown in Fig. 5. Thermotropic LCPs show domains of nearly perfect parallel alignment [11], whereas Parmax shows worm-like aggregates of the type seen in Fig. 5.

The rheological models for different types of macromolecules are extensively described in the literature. The rheology of flexible chain polymers is known to be dominated by chain reptation in a tube, i.e. the lateral motion of the flexible chain is constrained by the entanglements [12]. The rheology of thermotropic liquid crystalline polymers is thought to be determined by the macroscopic flow of the anisotropic nematic cholesteric or smectic domains of nearly perfect alignment [9, 13, 14]. An example of the morphology of LCPs and LCP PC blends is shown in the well-known book on polymer microscopy by Sawyer and Grubb [15]. In blends of LCPs with flexible chain polymers, the rigid rod-like polymers have a strong tendency to self-aggregate. But with the introduction of specific interactions between rigid-rod reinforcement and the matrix, molecular dispersion could be achieved, leading to a dramatic change in the flow properties [16]. The folding and unfolding kinetics of a semi-flexible polymer chain is studied by Sakaue and Yoshikawa [17] leading to crystalline rod and torroid structures below a transition temperature.

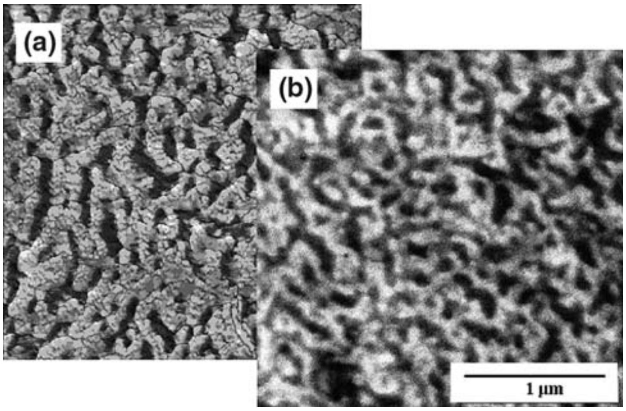

**Fig. 5** Micrographs of a microtomed cross section of compression-molded samples: (**a**) AFM image of Parmax 1200 and (**b**) TEM image of Parmax 1200

None of the rheological models described above covers the morphology as shown in Fig. 5. The rheological behavior of a morphology as shown in Figs. 3 and 4 seems to be determined by the worm-like aggregates slipping past one another. This is almost like the reptation of single flexible molecules, i.e. a kind of co-operative or macro-reptation. This could explain the resemblance of the viscoelastic behavior to flexible chain polymers.

The AFM micrographs of the Parmax 1200/BPA-polycarbonate blends (Fig. 6) show that the contrast in the AFM tapping mode is lost with increasing amounts of polycarbonate. A possible explanation might be that the flexible polycarbonate molecules fill up the free volume between the Parmax aggregates. This would also explain the compatibility of Parmax with other flexible chain polymers. The thermodynamics of these blends cannot be described by means of Flory-Huggings-like theories [10].

Blends of thermotropic liquid crystalline polymers and conventional thermoplastics have been intensively studied in the past two decades. It was found that an addition of LCP into an isotropic polymer at a low LCP concentration may lead to a drastic reduction in viscosity [18]. This effect has been attributed to the deformation of the LCP domains [19] or to interlayer slipping effects [20]. Hsieh et al. [21] suggested that the enhanced alignment and lubrication of LCPs at the molecular level are responsible for the synergistic flow behavior and low viscosity of a miscible LCP/polycarbonate blend. In all cases, the miscibility between the semi-flexible and the random-coil-like polymer was considered to be an important factor affecting the rheological behavior of the blends.

Figure 7 shows the viscosity of Parmax 1200/Makrolon M2800 blends as measured in oscillatory rheometry. We made these blends from NMP solution. The blends with up to 10% Parmax in M2800 do not show any significant increase in viscosity. This is in contrast to the results of Zhao et al. [18], who found that blends of a semi-flexible liquid crystalline polyester and polycarbonate at low LCP concentration show a very large reduction in viscosity as compared to the pure polycarbonate.

The blends with 20 and 50% Parmax show an increased viscosity. The increase in complex viscosity at high frequencies might be due to the fact that the measurement temperature in this region is relatively close to the glass transition temperature of both Parmax $T_g$ = 152 °C and polycarbonate $T_g$ = 145 °C. Again these results show that substituted poly(*p*-phenylene) behaves completely differently from known liquid crystalline polymers.

To attain a deeper insight into the structure property relationships of the blends, X-ray diffraction measurements were performed. The maximum in Fig. 8 gives the average lateral distance between two chains of about 0.515 nm in polycarbonate and about 0.445 nm in Parmax 1200. The width of the polycarbonate peak is considerably smaller than that of Parmax 1200. The width of the peak for the Parmax/PC blends does not change dramatically, i.e. the morphology of polycarbonate within the blend does not seem to change much. The X-ray diffraction diagrams of the 50/50 blend before and after annealing at $T$ = 200 °C are almost identical, i.e. the morphology of the sample made from solution did not change after annealing at $T$ = 200 °C. The hypothesis that polycarbonate fills up the free volume between the worm-like Parmax structure does not seem to be contradicted by these X-ray results.

The rheology of the Parmax polycarbonate blends illustrates that the rheology of Parmax is totally

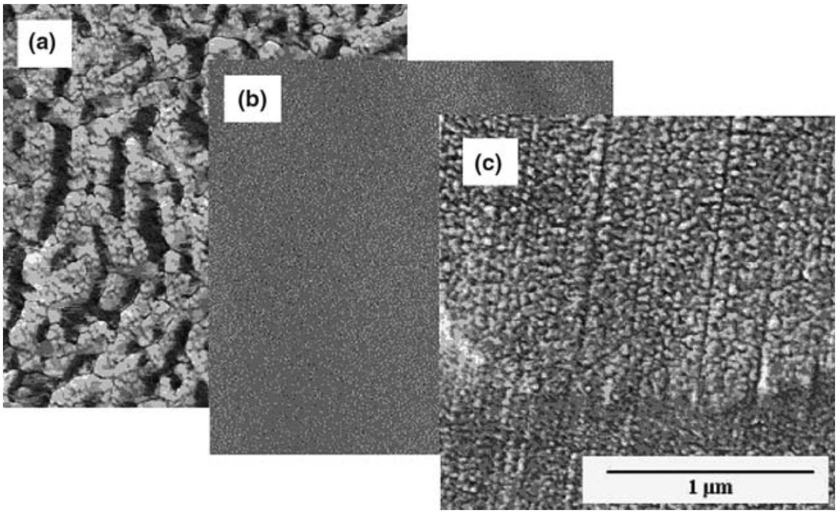

**Fig. 6** AFM images of cross sections of NMP solution cast films of (**a**) pure Parmax 1200, (**b**) pure Makrolon M2800 and (**c**) Makrolon M2800/Parmax 1200 50:50 blend, after annealing at 200 °C

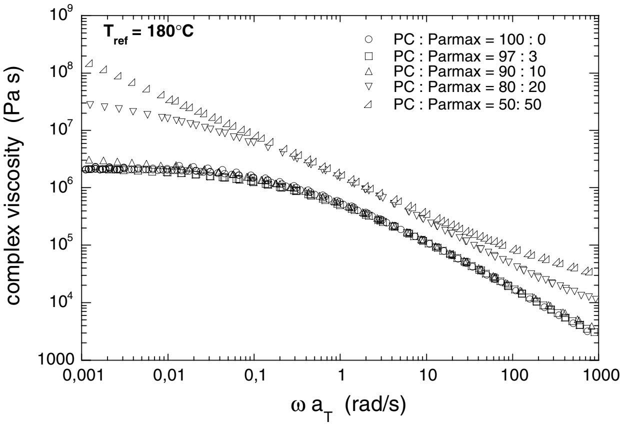

**Fig. 7** Viscosity of Parmax 1200/Makrolon M2800 blends measured in oscillatory shear as a function of the angular frequency ($T_{\mathrm{ref}}$ = 180 °C)

different from that from known for LCP thermoplastic blends. The reason might be the relatively high molecular weight of the Parmax sample. GPC coupled with viscometry in o-DCB was used to get an indication of the molecular weight of the Parmax sample. A molecular weight of about $M_n = 1.52 \times 10^4$ kg/kmol, $M_w = 6.19 \times 10^4$ kg/kmol was found by polystyrene calibration. The real (absolute) molecular weight might be considerably smaller, as indicated by the Staudinger index found from viscometry, but nevertheless much higher than usual for LCPs.

## Conclusion

The rheological properties of Parmax 1200, a semi-flexible substituted polyphenylene, were investigated. The reported high stiffness of the material was confirmed. The rheological measurements proved that, despite the very high stiffness of the molecules, Parmax showed shear thinning and that, although the viscosity is very high and the melt is highly elastic, the polymer can be extruded in the melt.

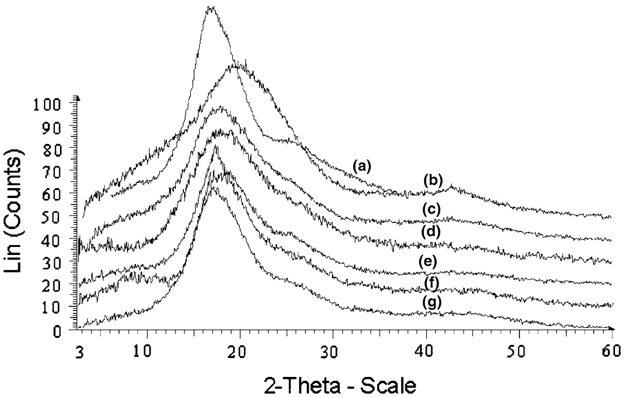

**Fig. 8** X-ray diffraction spectra of (**a**) pure polycarbonate with a peak at 0.515 nm, (**b**) pure Parmax 1200 with a peak at 0.445 nm, (**c**) PC/Parmax blend 50:50 after annealing at 200 °C, (**d**) PC/Parmax blend 50:50, (**e**) PC/Parmax blend 80:20, (**f**) PC/Parmax blend 90:10, (**g**) PC/Parmax blend 97:3

A worm-like morphology was detected in AFM and TEM. This morphology could explain the reported mechanical and rheological behavior. The compatibility with flexible chain polymers (e.g. polycarbonate) could also be explained by the worm-like morphology. The flexible chains are not compatible on a molecular scale, but occupy the free volume in between the worm-like morphology on the submicron scale.

Parmax seems to be a new class of polymeric material. Its behavior and morphology are completely different from that of flexible or liquid crystalline polymers.

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