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Solution properties and kinetics of aggregation of an alkyl-substituted poly(*p*-phenylene)

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Dedicated to the memory of Professor Dr. Tadeusz Pakula.

Abstract

Freshly prepared solutions of poly(2,5-di-*n*-dodecyl-1,4-phenylene) (PPP 12) in toluene are metastable at room temperature with regard to a process which leads to the formation of aggregates composed of up to 100 individual macromolecules. This aggregation process has an induction period of more than 10 h at room temperature. The kinetics of aggregation was investigated by making use of a fast capillary membrane osmometer. Aggregation follows an Avrami–Evans type formalism and suggests that clusters of a lyotropic liquid crystalline phase of the polymer are formed of the same type as observed in the melt. The long induction period of aggregate formation in dilute solution in toluene allows to apply conventional techniques of molar mass determination like membrane osmometry and size-exclusion chromatography (SEC). A relationship $[\eta] = 1.94 \times 10^{-3}\ \mathrm{M}^{0.94}$ was found for PPP 12 in toluene at 20 °C and a persistence length of 15.6 nm was derived applying the Bohdanecky-formalism. This gives evidence of the worm-like nature of the non-aggregated PPP 12 in dilute solution.

Keywords: Poly(*p*-phenylene); Persistence length; Osmometry

1. Introduction

Rigid-rod type polymers have received much attention because of their materials' properties which arise from the anisometric shape of the macromolecules, and they have been considered as building blocks of supramolecular architectures [1]. Generally speaking all polyconjugated macromolecules fall into this class of polymers. Poly(*p*-phenylene) (PPP) is a typical representative but other polymers like poly(diacetylene)s, poly(pyrrole)s, poly(thiophene)s and poly(fluorene)s are worth mentioning just to give a few more examples.

Unsubstituted polyconjugated macromolecules are all insoluble. They need to be functionalized to increase their interaction with potential solvents. Attaching flexible side chains to the repeat units has proven to be a concept of general value to achieve solubility of these polymers in ordinary solvents and even to allow melt-processing of most representatives. The presence of flexible side chains increases the configurational entropy of the macromolecules in the transition from the solid to the liquid (or solvent diluted) state while the configuration of the backbone trajectory remains largely unaffected [2]. However, in the context of general theory of macromolecular substances and more specifically in the context of molecular electronics it is of interest to know what the residual flexibility of the backbone trajectory is like in dilute solution when all intermolecular contacts are screened by the solvent. It is to be anticipated that all of these polymers can be described as worm-like following the original concept developed by Kratky and Porod [3]. This asks for the determination of the persistence length as the characteristic magnitude which describes the flexibility of the otherwise undisturbed chain in thermal equilibrium.

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Experimental data on the persistence length of hairy rod type polymers are scarce and difficult to obtain [4−6]. Attempts to determine the intrinsic solution properties depending on chain length suffer frequently from poor reproducibility because of time dependent aggregation phenomena which seem to occur in many, or even most, of these systems. In the case of alkyl-substituted poly(*p*-phenylene)s (PPP) **1** (Fig. 1) all attempts to determine molecular weights by absolute methods have been hampered by aggregation phenomena of yet unknown nature. These give rise to e.g. increase of scattering intensity from dilute solutions depending on the history of the solution under study. Here, the term history refers to the temperature protocol obeyed in the dissolution process and the time scale involved in the measuring procedure. Sometimes and depending on the detailed structure of the backbone elements this leads to the observation that the UV−vis absorption spectra undergo dramatic changes depending on temperature and time when the polymers are studied under dilute or semi-dilute conditions [7−11].

If we restrict the discussion to PPP and its derivatives, it needs to be mentioned that the polymer **3** has been extensively characterized in dilute solution [12,13]. The somewhat complex substitution pattern and sterical hindrance induced by the bulky di-*tert*-butylphenyl side groups render this polymer soluble in all common organic solvents. Aggregation in dilute solution has never been observed while formation of a lyotropic liquid crystal phase is seen in highly concentrated solution. A persistence length of 12.6 nm was observed for this material. However, when polymer **3** was converted into the free sulfonic acid and/or in its salts, the formation of well-defined cylindrical micelles in water was observed. They represent a specific situation of aggregation which has been investigated in much detail [14−17].

Similar types of aggregation have been observed very recently by Findenegg et al. [18,19] who have investigated a water compatible non-ionogenic representative of a PPP, which gave cylindrical micelles as well.

In the following we wish to describe the solution behavior of the non-polar PPP 12 (**2**) as a model representative for alkyl-substituted polyconjugated macromolecules. Like all alkyl-substituted PPPs it shows a thermotropic liquid crystalline phase, given that the degree of polymerization surpasses a critical length [20]. The structure and rheology of this material depending on molecular weight have been studied in detail [21,22]. Such studies became possible because the material is readily available at different molecular weights by established synthetic schemes employing the Suzuki coupling reaction between a dialkyl-*p*-bromobenzene and the corresponding dialkyl-bis-boronic-acid ester [23,24].

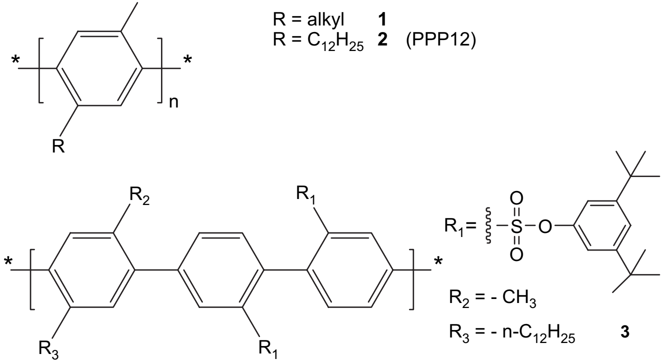

Fig. 1. Structures of the poly(*p*-phenylene)s discussed in this work.

2. Experimental

PPP 12 was synthesized as described by McCarthy et al. [21], and a series of polymers differing in molecular weights (see Table 1) were obtained. All polymers had been subjected to end capping with bromobenzene to avoid boronic acid end groups. The latter may cause aggregation via end group association.

Solutions for polymer characterization were prepared by dissolving the material in boiling toluene, followed by filtration of the hot solution through a glass sinter plate to remove dust particles. The hot solution was then rapidly quenched to room temperature within the shortest possible time.

Membrane osmometry was carried out with a self-built osmometer characterized by a response time of not more than 15 s. The osmometer was designed by Köhler et al. [25,26], and had a concentric design with the membrane in the form of a hollow fibre capillary. The cell volume was 12 μL. The molar mass cutoff was below 5 kg mol^{-1}. Details of the design and performance of this instrument including the membrane material have been described previously [25,26]. All measurements were performed at 20.0 ± 0.1 °C. The time necessary to achieve pressure equilibrium was less than 1 min when the resulting osmotic pressure was recorded against the pure solvent.

Size-exclusion chromatography (SEC) was performed with freshly prepared solutions in toluene using the same procedure as for osmometric measurements. A combination of 3 styragel columns (porosity 103, 105, 106) with a UV detector operating at 254 nm was used at a flow rate of 1 mL min^{-1}. The elugrams were calibrated making use of the data reported by Vanhee et al. [12] for the PPP **3.**

Intrinsic viscosities were determined in toluene at 20.0 °C with an Uhbelohde type capillary viscometer.

Table 1
Characteristic data of PPP 12 (Samples A−L) obtained in toluene at 20 °C

Sample	Osmometry M_n (kg mol^{-1})	Viscometry $[\eta]$ (mL g^{-1})	SEC[a] M_n (kg mol^{-1})	M_w (kg mol^{-1})
A	5.8	3	5.1	9.6
B	12.1	14	8.6	16.0
C	13.2	20	11.7	21.9
D	14.9	26	13.4	24.3
E	16.4	25	16.5	29.3
F	19.4	36	17.1	33.2
G	21.4	51	21.2	40.5
H	24.5	50	24.4	46.6
I	29.1	58	25.9	64.6
K	35.6	71	36.6	92.2
L	42.3	91	47.9	108.7

[a] SEC data calibrated against polymer **3** as standard (see Ref. [12]).

3. Results and discussion

PPP 12 dissolves in boiling toluene. When the solutions are rapidly quenched to room temperature they seem to be stable. However, preliminary light scattering experiments indicated that the scattering intensity starts to grow after several hours and eventually within a day turbidity develops which can be detected by naked eye.

As we had an osmometer at hand which had an ultra fast response time it was decided to investigate the kinetics of aggregation by monitoring the time evolution of the osmotic pressure. The time necessary to filtrate the hot toluene solution, transfer it to the sample chamber of the osmometer, and obtain the first osmotic equilibrium measurement amounts to somewhat less than 2 min. As will be shown below, solutions of PPP 12 at concentrations $c \leq 10\ \mathrm{g\,L^{-1}}$ are stable at 20 °C for about 10 h whence aggregation starts to occur spontaneously. The osmotic pressure π was, therefore, evaluated according to

$$\lim_{c\to 0}\frac{\pi}{c} = \mathrm{R}T\left(M_\mathrm{n}^{-1}\right) + A_2 c \tag{1}$$

R is the gas constant, T is the temperature, M_n is the number average molar mass, A_2 is the second virial coefficient. A_2 was found always to be positive but of such small magnitude that the second term in Eq. (1) can be neglected at concentrations $c \leq 10\ \mathrm{g\,L^{-1}}$. The data obtained for 11 different samples of PPP 12 (samples A–L) are listed in Table 1. It follows that the samples cover the range of $5\times 10^3 \leq M_\mathrm{n} \leq 45\times 10^3\ \mathrm{g\,mol^{-1}}$. Once it was known from these experiments that freshly prepared solutions of PPP 12 have a time lag with regard to the onset of aggregation it became feasible to try SEC as a means to determine molar mass distributions. In fact, reproducible data could be obtained when the solutions in toluene had been freshly prepared as described above and if they were injected into the SEC immediately.

SEC is a relative method of molar mass determination. It needs an appropriate standard to convert the elugrams into molar mass distributions. Poly(styrene) which is frequently used as a standard is not useful here. PPP 12 is to be characterized as a worm-like (“Kratky–Porod”) chain, while poly(styrene) is a classical polymer of high chain flexibility. However, polymer **3**, a poly(*p*-phenylene) with both aliphatic side chains and polar sulfonate ester groups had been recently characterized with regard to its solution properties as typical worm-like [12]. The data obtained by SEC from PPP 12 were thus calibrated against this standard, and the results for the 11 different samples are compiled in Table 1. A comparison of the M_n data obtained by osmometry and by SEC shows excellent agreement. Further the ratios of weight average molar masses M_w and M_n, that is the polydispersity, range between 1.8 and 2.5. This agrees with expectations one may have considering the mechanism of polycondensation by which the samples are obtained [24].

The number average degrees of polymerization P_n are thus found between 12 and 110 corresponding to contour lengths ℓ of the chains between 5 and 47 nm. The persistence length of PPP 12 can be determined measuring the intrinsic viscosities $[\eta]$ of samples of known M_w. The Mark–Houwink–Sakurada Eq. (2) is generally accepted to represent the dependence of $[\eta]$ of a polymer solution at given temperature and in a given solvent on the molar mass.

$$[\eta] = KM_\mathrm{w}^{\alpha} \tag{2}$$

K and α are constants. Their average values for PPP 12 in toluene were found as $K = 1.94\times 10^{-3}\ \mathrm{mL\,g^{-1}}$ and $\alpha = 0.94$. The magnitude of the exponent α close to 1 points already into the direction of the worm-like character of PPP 12 [27]. In consequence, PPP 12 may be represented as having a backbone of 1,4-linked phenylene rings with fluctuating curvature where the side chains act as attached “solvent molecules”. The magnitude of the curvature and, thus, the stiffness of the chain is characterized by the persistence length a. The latter is defined by

$$\langle \cos\phi \rangle = \exp(-\ell/a) \tag{3}$$

where ϕ is the angle between two arbitrarily chosen repeat units (i.e. the director axes of the 1,4-linked phenyl rings) separated by the contour length ℓ. An approximation for the $[\eta]$–M relation in terms of the worm-like nature of the dissolved chains has been derived by Bohdanecky [28] from which the magnitude of the persistence length can be extracted according to

$$[\eta] = M_\mathrm{w}^2\left(A_\eta + B_\eta M_\mathrm{w}^{1/2}\right)^{-3} \tag{4}$$

A further characteristic magnitude to be derived from this data set is the hydrodynamic radius of the chain d_r.

According to Bohdanecky the following relations hold

$$a = \frac{M_0}{2\ell_0}\,\frac{B_0^2}{B_\eta^2\phi_0^{2/3}} \tag{5}$$

and

$$\frac{d_\mathrm{r}}{A_0} = \frac{4\phi_0^{2/3}\bar{\nu}B_\eta^4}{1.215\pi N_\mathrm{A}A_\eta} \tag{6}$$

with

$$\log\left(\frac{d_\mathrm{r}^2}{A_0}\right) = 0.173 + 2.158\log\left(d_\mathrm{r}\right) \tag{7}$$

M_0 is the molar mass of the repeat unit ($440\ \mathrm{g\,mol^{-1}}$) of length ℓ_0 (0.426 nm). $B_0 = 1.05$ and ϕ_0 is the viscosity constant for infinite chain length ($2.86\times 10^{23}\ \mathrm{mL^{-1}}$). A_0 is a function of d_r as defined by Eq. (7) and $d_\mathrm{r} = d/2a$ is the reduced hydrodynamic diameter of the chain of cross diameter d. $\bar{\nu}$ (approximated as 1) is the partial specific volume of the polymer in solution. N_A is the Avogadro’s number.

Fig. 2 shows a plot of the experimentally observed data of the intrinsic viscosities vs. the weight average molar masses of

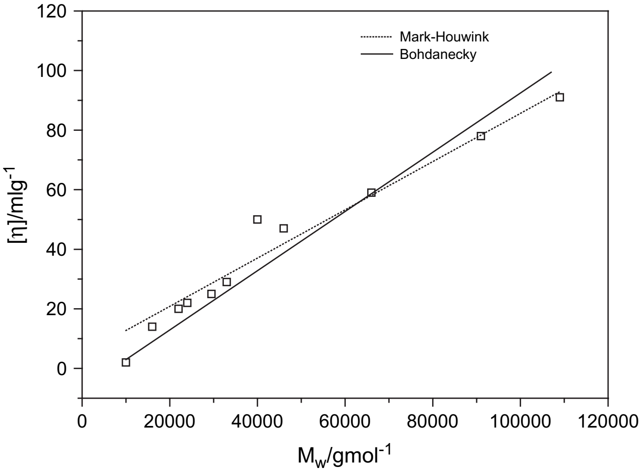

Fig. 2. Intrinsic viscosity against molar mass for the polymers A–L (c.f. Table 1) in toluene at 20 °C. For explanation of the solid and broken line (see text).

the different samples of PPP 12 (c.f. Table 1). Note that the difference between the viscosity average molar mass M_η of the polydispersed samples and the weight average molar mass M_w is neglected which is permissible in the present case, because the exponent α in Eq. (2) is close to unity. This makes the difference between the two averages negligibly small. The same argument holds for Eq. (4), where an even more complicated averaging is involved.

The broken line through the data points in Fig. 2 gives the best fit in terms of Eq. (2) with $K = 1.94 \times 10^{-3}$ mL g^{-1} and $\alpha = 0.94$; the full line represents the best fit according to Bohdanecky with $A_\eta = 184$ g mol$^{-2/3}$ mL$^{-1/3}$ and $B_\eta = 0.92$ g mol$^{-1/6}$ mL$^{-1/3}$. The persistence length is calculated from these data and Eq. (5). It has a magnitude of 15.6 nm. The hydrodynamic diameter d_r is 1.6 nm. The slight discrepancy between the fits according to Eqs. (2) and (4) may be due to the above assumption that the difference between viscosity and weight average can be neglected. However, there is also a scatter of the data points which does not allow to draw better conclusions at this time.

These data may be compared in Table 2 with the equivalent data of the polymer **3** which have been obtained previously [12] using the same approach. It is pleasing to see that approximately the same behavior is found for the two polymers which exhibit the same backbone but differ strongly with regard to the structure of the side chains. This indicates – not unexpected – that the hydrodynamic behavior of the individual chains is dominated by the flexibility of the backbone elements. The fact that the persistence length of PPP 12 is by approximately 20% larger than that of polymer **3** may be a consequence of the substitution pattern, i.e. sterical hindrance of chain bending fluctuations by the sterically more crowded situation in PPP 12 as compared to **3**. Note that in PPP 12 each phenylene unit carries two large aliphatic substituents whereas polymer **3** has a less crowded substitution pattern. This explanation is consistent with Monte-Carlo calculations on the average conformation of the chain segments of PPP 12 which have been reported elsewhere [22].

It is further worth noting that the value of α, the exponent in the Mark–Houwink–Sakrada equation, is the same within the limits of error for the two polymers which proves the point that polymer **3** is a reasonable standard to calibrate the SEC for worm-like polymers.

4. Aggregation phenomena

The fast capillary membrane osmometer [25,26] used to determine the number average molar mass of the freshly prepared polymer solutions provides the means to study aggregation phenomena in real time. As was mentioned above, the second virial coefficient is so small for solutions in toluene that Eq. (1) can be rewritten as

$$M_\mathrm{n,ap} = \frac{\mathrm{R}Tc}{\pi} \tag{8}$$

$M_\mathrm{n,ap}$ is here the apparent number averaged molar mass of the sample undergoing aggregation in the course of the measurement. The value obtained from the freshly prepared solution at time $t = t_0$ is now referred to as M_0. In the course of time the number average aggregation number $Z_\mathrm{n} = M_\mathrm{n,ap}/M_0$ is reached. Z_n is inversely proportional to the averaged reduced particle concentration $c_\mathrm{r} = c/c_0 = Z_\mathrm{n}^{-1}$.

Fig. 3 shows a typical result obtained in this way. Here, the development of Z_n with time is shown for a solution of PPP 12 (sample K in Table 1) in toluene. It now becomes obvious that aggregation starts only after a long delay time, that is nucleation period of more than 10 h in which no change of Z_n and therefore $M_\mathrm{n,app}$ is observed.

Once the nucleation has occurred, a fast increase in Z_n is seen but still at a rate which allows to monitor the process by the osmometer with its own time of resolution of somewhat less than a minute. Very large aggregation numbers are reached after several days when the limits of detectability are reached at $Z_\mathrm{n} \geq 100$. In order to study the dependence of this aggregation on the initial concentration, the experiments reported in Fig. 4 were undertaken. It shows the development of the reduced concentration c_r with time for toluene solutions of PPP 12, sample

Table 2
Comparison of relevant magnitudes which characterize the hydrodynamic behavior of poly(p-phenylene)s **2** (PPP 12) and **3**

Polymer	A_η[a] (g mol$^{-2/3}$ mL$^{-1/3}$)	B_η[a] (g mol$^{-1/6}$ mL$^{-1/3}$)	K[b] (mL g^{-1})	α[b]	a[c] (nm)	Ref.
2 (PPP 12)	184	0.92	1.94×10^{-3}	0.94	15.6	This work
3	111	0.86	2.67×10^{-3}	0.96	12.6	[12]

[a] c.f. Eq. (4).
[b] c.f. Eq. (2).
[c] Persistence length, c.f. Eq. (5).

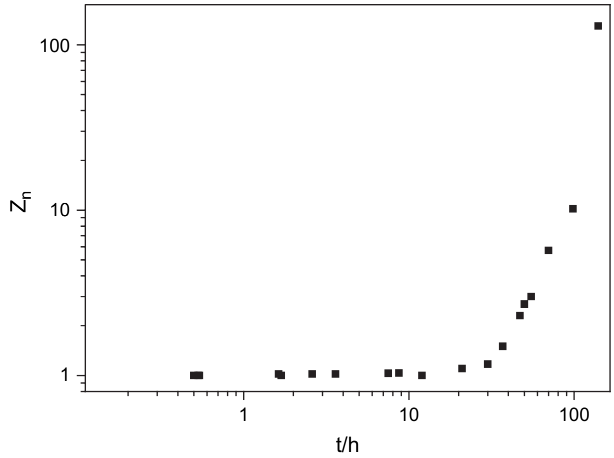

Fig. 3. Number averaged apparent aggregation number Z_n observed by Osmometry as function of time for sample L (c.f. Table 1) in toluene at 20 °C. Note that Z_n starts to build up after an induction period of more then 10 h.

F (Table 1) at three different concentrations. Once again the long nucleation period becomes visible followed by a fast non-linear aggregation process. The length of the induction or nucleation period seems to be slightly dependent on concentration and decreases as the concentration increases.

The solutions as prepared in toluene by fast quenching from high temperature to the ambient temperature are obviously in a metastable situation. A phase change occurs whenever a sufficient number of nuclei are formed. Thus a treatment of the available data in terms of the kinetics of phase changes following an Avrami–Evans formalism [29,30] seems to be appropriate. The concentration of growing particles $c_t = c_r\,(t)$ is given by

$$c_t = c_0 \exp - (kt)^b \tag{9}$$

The parameter k is the time constant of the process, and the exponent b depends on the shape of the growing particle and contains information on the time-law of the formation of the nuclei, for instance whether they form instantaneously or follow a specific rate law. If there is no sudden change in the rate of nucleation nor in the form of the growing particles (aggregates) as the concentration is changed, then one should be able to construct a master curve which describes the concentration independent nature of the aggregation. This is in fact true as is demonstrated by Fig. 4 which shows the aggregation kinetics observed for sample F (Table 1) in the appropriate coordinates.

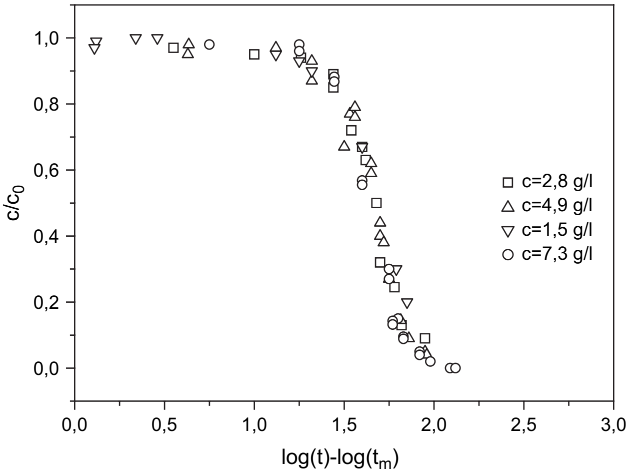

Fig. 4. Master curve describing the growth of the aggregates of PPP 12 (sample F) (see text).

The Avrami–Evans parameters k, b and the induction time t_i that is the time lag after which the first increase in Z_n is seen have been determined for the samples F, G and K.

The time constant k was found to be strongly dependent on the initial polymer concentration c_0, but it was independent on the degree of polymerization of these three samples. The values for k were found to vary between 155^{-1} (at $c = 1\ \mathrm{g\,L^{-1}}$) and 485^{-1} (at $c = 7.2\ \mathrm{g\,L^{-1}}$) approximately following ac^{-1} relationship (not shown here). A linearization of the data according to Eq. (9) gave values of the exponent $2.4 \leq b \leq 2.9$, again independent of the degree of polymerization. Similarly, the induction period for aggregation did not depend on the degree of polymerization but solely on concentration in each of the three cases studied. It was larger than 10 h even at the highest concentration of 11 $\mathrm{g\,L^{-1}}$.

Thus, master curves can be constructed which remove the effect of concentration by scaling the experimentally observed magnitude of the reduced particle concentration with the reduced time t/t_m. Here t is the actual time of the aggregation process at each concentration and t_m is the respective time observed at the highest concentration. An example of such a master curve is shown in Fig. 4 for sample F.

The magnitude of the exponent b and its independence on degree of polymerization and concentration points into the direction that the aggregates are all of the same shape and form and they must grow following the same mechanism. A value of 3 for the exponent would indicate that particles of spherical shape are formed following a thermal nucleation process [29]. Values for b significantly smaller than 3 would point towards aggregates of more disc-like shape and/or to a more complex time-law of nucleation.

In the light of these uncertainties we have tried to identify the nature and shape of the aggregates employing electron microscopic methods. Such attempts were based on the consideration that the fact that the Avrami–Evans formalism can satisfactorily describe the kinetics of aggregation indicates that one may deal with crystallization of the polymers from dilute solution [30]. However, evidence for formation of crystals of the polymers could not be found employing the methods commonly used, e.g. in preparation of single-crystals of poly(ethylene) from dilute solutions [30,31]. Transmission electron microscopy revealed poorly defined and highly irregular objects. They seemed to be artefacts of preparation and had no resemblance to what one might reasonably expect in the light of a process described by the Avrami–Evans formalism (e.g. particularly of the same size and shape). On the other hand it is known that worm-like polymers of the type investigated here and similarly poly(diacetylenes) which also belong to the class of worm-like polyconjugated polymers, all exhibit lyotropic liquid crystalline phases [20,32,33]. These phases are characterized by a lamellar morphology with the chain

Fig. 5. Transmission electron micrograph of a thin film of PPP (sample G) quenched to room temperature. Formation of a crack pattern revealing the strain distribution in the sample and formation of crazes is revealed (see text).

directors normal to the lamellar plane and the thickness of the lamellae corresponding to the length of the macromolecules. This could, therefore, imply that the aggregation phenomena seen to occur in solution are nothing else but the onset of the formation of lyotropic droplets in the regime of coexistence between the isotropic and the *lc*-phase. Further work is necessary to prove that point. In any case, Fig. 5 shows the morphology of a thin film of polymer G (Table 1) in terms of an electron micrograph which reveals the liquid crystalline nature of the materials in the bulk.

Evaporation of solvent from the film and quenching to low temperature have caused the development of fracture zones. These fracture zones follow the director field of the mechanical strain in the material subject to its liquid crystal texture. The fracture zones in this micrograph reveal the presence of two disclinations of strength $s = 1/2$ and $s = -1/2$. One should also note that the fracture zones are bridged by material in the form of fine fibrils similar to what can be observed in materials that show mechanical failure by development of crazes. The diameter of these fibrils scales reasonably well with the contour length of the polymer.

5. Conclusions

Poly(2,5-di-*n*-dodecyl-1,4-phenylene) (PPP 12) may be considered as a prototypic polyconjugated polymer which undergoes reversible aggregation in organic solvents. It is completely soluble at high temperature in, e.g. toluene, but starts to aggregate if the dilute solutions are brought to ambient temperatures. The aggregation process can be described by an Avrami–Evans type formalism with an induction period long enough to allow precise determination of molar mass and chain conformation of the non-aggregated macromolecules. These measurements prove the worm-like nature of the individual macromolecules. Determination of the persistence length corroborates earlier results on other polyconjugated polymers and characterizes these polymers as semi flexible. While the size of the aggregates and their time evolution can be precisely determined by osmometric measurements their form and internal structure remains a puzzle. Attempts to obtain real space images of these objects by TEM-methods failed. However, based on evidence from previous work that PPP 12 and similar polymers exhibit lyotropic liquid crystal phases it is speculated that it is the onset of the formation of lyotropic droplets in the biphasic regime of the equilibrium between the isotropic and lyotropic phases in the binary system polymer/solvent that is detected and named ‘‘aggregation’’.

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