

Dynamics of Flexible Polymer Chains in Elongational Flow

Tuan Q. Nguyen*

Abstract: This paper focuses on the recent developments achieved in our group in the field of flexible polymer chain dynamics in elongational flow. Stress-induced orientation and deformation in flowing polymer solution is being surveyed in a wide variety of manifestations. Two types of flow fields have been investigated: the opposite-jet flow with a stagnation point, and the abrupt contraction flow with open flowlines. Emphasis has been placed on the latter geometry due to its widespread occurrence. Degradation experiments performed with dilute PS solutions in abrupt contraction flow demonstrate a distinct propensity for midchain scission, a feature apparently consistent with highly extended chains. On the other hand, the critical strain-rate for chain fracture ($\dot{\epsilon}_f$) determined under the same experimental conditions scales with M^{-1} . The inverse relationship with polymer MW is characteristic of partly uncoiled chains but not of highly extended chains, for which a stronger MW dependence ($\dot{\epsilon}_f \propto M^{-2}$) is expected. The 'yo-yo' model, which could rationalize these findings, is refuted by fluorescence depolarisation measurements which indicated that central orientation is more progressive than the average segmental orientation. For the first time, polarization-modulated birefringence was used to determine the state of local chain orientation in abrupt contraction flow. Axisymmetric contraction flow is complicated by the large variations in local molecular orientation along different streamlines. To account for this effect, a numerical inverse Abel transform has been devised to compute local birefringence (Δn) from experimental retardation (δ). Results show a steep decrease in birefringence with axial distance. Birefringence profiles determined in a direction perpendicular to the flow show a maximum, not at the centre, but in the vicinity of the orifice walls. This observation is in accord with flow simulation results which indicated the presence of extreme strain rates near re-entrant corners. Molecular extension ratios calculated with the Kuhn-Grün theory gives a qualitative description of polymer uncoiling up to about one third of the chain contour length at the approach of capillary entrance. A notable departure from the affine deformation model is, however, observed with multiple birefringence saturation levels changing with flow rate conditions. This behaviour could be explained by the presence of transient molecular conformations. Efforts are underway to visualize these metastable states by single chain fluorescence video microscopy using UHMW polystyrene randomly grafted with anthracene chromophores.

Keywords: Dilute PS solution · Flow birefringence · Flow-induced degradation · Fluorescence depolarisation · Single-chain visualization

1. Introduction

Characterization has become an unavoidable step in any quantitative investigation of polymer materials. Along with mechanical and physical characterization (presented elsewhere in this special issue

of CHIMIA), our laboratory has a long experience in the field of physicochemical analysis. Over the years, expertise has been gained in several domains which embrace a number of specialties extending from flow field modelling, rheo-optical spectroscopy to chromatographic separation. With the increasing awareness on the importance of polymer characterization in both fundamental and applied research, our group is frequently requested to provide technical support for a broad range of polymer analysis problems. New methodologies have been developed to characterize molecular weight distribution of UHMW macromolecules, chain branching in sparingly soluble plastics and morphology changes of

semicrystalline polymers by optical spectroscopy.

Due to length limitation, only flexible polymer chain dynamics, which constitutes an important subset of our research on polymer characterization, will be discussed in detail in this paper. Although the main motivation for our study is a basic understanding of the process of polymer chain orientation and deformation in flowing systems, the information gained is fundamental to a molecular interpretation in many important applications, such as rheological measurements, polymer processing, fibre technology, mechanochemical degradation, flow through porous media, drag reduction and other non-Newtonian flow behaviours.

*Correspondence: Dr. T.Q. Nguyen
Laboratoire de Polymères (DMX-LP)
Département des Matériaux
Ecole Polytechnique Fédérale de Lausanne
EPFL-Ecublens
CH-1015 Lausanne
Tel.: +41 21 693 28 49
Fax: +41 693 58 68
E-Mail: tuan.nguyen@epfl.ch

2. Flexible Polymer Chain Dynamics

Chain uncoiling in flow is an intricate process which depends markedly on the details of the flow field. Only flow of low vorticity can induce substantial chain deformation [1]. Principally two types of elongational flow (EF) have been used in this work: the opposite-jet flow with a stagnation point, and flow through an abrupt contraction with open streamlines (Fig. 1). Emphasis has been placed on the latter geometry due to its widespread occurrence. Abrupt contraction (also known as transient elongational) flow is ubiquitous and could be found in a number of industrial processes like pumping, filtering, flow through porous media, between spherical beads as in chromatographic columns, extrusion and fibre spinning. A fluid impinging on a surface, flow around a corner, near an obstacle, at a contraction, before and after a bifurcation, or through porous media all possess some transient elongational component [2]. In addition, several practical phenomena fulfil the criterion for transient elongational flow, like microeddies in turbulent liquids with accompanying drag reduction phenomena [3] and bubble implosion in cavitation collapse [4]. Because of the difficulties in reaching steady state in most shearfree flow, transient shearfree flows of polymeric liquids are very important. In fact, it is practically impossible to create steady EF and any EF is, by definition, transient in nature. In some specifically designed geometries with a stagnation point, it is possible to create a very narrow region where flow could be considered as 'quasi-steady' elongational. These regions of limited extension are surrounded by large region of transient EF. Another complication with EF is the presence of bound surfaces which introduces shearing in any experimental realization. Difficulties in creating an elongational flow field with reasonable spatial extent and uniformity were the main reason which hampered research in that field.

A single polymer chain immersed in a flowing solvent is an entity of utmost complexity. Study of its deformation necessitates a combination of analytical tools to probe specific features of the uncoiling process. Chromatographic, rheo-spectroscopic and flow simulation methods have been used in the course of this investigation. Some unique instruments, such as a laser-based polarization modulated fluorimeter, have been developed or adapted from existing commercial instruments (spatially resolved birefringence

polarimeter, single-chain observation video microscopy). The topic is multidisciplinary and encompasses separate research areas, unified under the common theme of molecular conformation under stress.

2.1. Flow-Induced Chain Scission

Shear-induced chain scission constitutes a fundamental obstacle in a number of polymer applications such as turbulent drag reduction, filtering, extrusion, characterization of ultra-high MW polymers in solution, and is probably one of the most distinctive features of abrupt contraction flow [2]. The phenomenon has already been investigated by Staudinger in the early days of macromolecular chemistry [5]. Although it was well-recognized that the propensity for flow-induced chain scission increases with polymer chain length, there was no real quantitative investigation until the early 80's and many contradictory results existed in the literature. In retrospective, one can recognize that most of the observed discrepancies could be traced back to the use of insufficiently characterized starting material (broad MWD) and uncontrolled flow geometry. Flow at the entrance of a capillary is mainly elongational and accounts for most of the degradation behaviour. This fact was not properly recognized for a long time and has led to frequent misinterpretation of the results [6]. Using opposite-jet flow, the group in Bristol demonstrated from flow birefringence measurements that chain scission occurred near the macromolecule centre above a critical strain-rate ($\dot{\epsilon}_f$) for bond fracture [7]. A few years later, Merrill and coworkers reported similar observation in abrupt contraction flow [8]. The

similarity of the results obtained from two groups in qualitatively different flow fields raised a number of questions concerning polymer conformation prior to bond fracture. In the opposite-jet geometry, the presence of a stagnation point should allow trapped macromolecules sufficient time to accumulate the required strain for large molecular extension. Indeed, the Bristol group has reported in a series of papers [9] that the critical strain rate for chain scission scales with polymer molecular weight as M^{-2} , in conformity with the theoretical prediction for fully extended chains [10]. To the difference of stagnation-point elongational flow, converging flow lacks a symmetry centre and has open streamlines. Although experimental strain rates can reach exceedingly high amplitudes ($>10^6 \text{ s}^{-1}$ in some instances), the residence time in the high strain rate region is limited to less than τ_z , thus imposing an upper limit to the degree of chain extension. Does the propensity for centre scission also mean that chains are fully extended in abrupt contraction flow? If this is correct, then the same scaling law should be obtained in both transient and quasi-steady EF. To verify this hypothesis, we have carried out a series of experiments using refracted PS standards dissolved in good and theta solvents [11], at different temperatures [12], concentrations [2] and jet geometries [13]. In accord with Merrill's results, sharp midchain scissions with relative standard deviations (σ) as low as 4% have been recorded in the good solvent 1-methyl-naphthalene. The precision of midchain decreases somewhat in a theta-solvent ($\sigma = 7\%$ in decahydronaphthalene, Fig. 2) and with increasing polymer concentration.

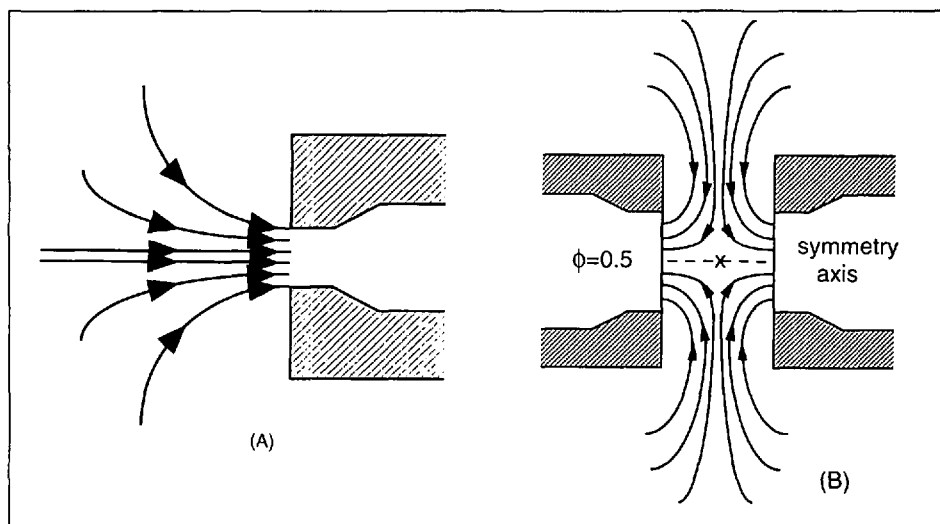


Fig. 1. Abrupt contraction and opposite-jet flow cell. The jet tips are made with synthetic sapphire with a 0.5 mm orifice diameter. The gap distance in the opposite-jet cell is adjustable from 0.1 to 2.0 mm.

The degradation yield (Φ) as a function of fluid strain rate and polymer MW are shown in Fig. 3. The number of degraded chains may reach 90% after a single passage across the contraction. The use of narrow polymer fractions permits a better determination of the onset of degradation and hence, of $(\dot{\epsilon}_f)$ which is observed to vary as the inverse of polymer chain length [14].

Surprisingly, the $(\dot{\epsilon}_f) \propto M^{-1}$ scaling law is found to be followed in a large number of mechanochemical degradation processes such as during solvent freezing [15] or ultrasonication of dilute polymer solutions [4]. To the best of our knowledge, M^{-2} dependence has been reported only in the previously cited case of opposite-jet flow degradation and this distinctive feature is frequently used as an argument to demonstrate that polymer chains are not only fully oriented but also fully extended in elongational flow [9].

2.2. Flow Birefringence in Abrupt Contraction Flow

Degradation experiments described in the preceding section demonstrate a distinct propensity for midchain scission in abrupt contraction flow, a feature apparently consistent with highly extended chains. On the other hand, the critical strain-rate for chain fracture $(\dot{\epsilon}_f)$ determined under the same experimental conditions scales with M^{-1} , a characteristic of partly uncoiled chains but not of highly extended chains [16]. Flow birefringence is a valuable technique for the investigation of molecular orientation and its application to converging flow may help to clarify this apparent contradiction.

A large amount of literature currently exists on the birefringence behaviour of flexible polymer chains in flows which possess a stagnation point, such as the four-roll mill [17][18], the cross-slot [19] or the opposite jets device [17][20]. Surprisingly, in contrast to the large number of studies devoted to abrupt contraction flow, the stretching behaviour of *isolated* macromolecules in this flow geometry has been studied in much less detail. As has been realized during this study, birefringence measurements in axisymmetric converging flows are much more complex than in stagnation point flows [21]. The first problem was the large variation in optical properties, both in the axial (x) and radial (r) directions, which necessitates a precise spatial mapping of the birefringence zone (Fig. 4). This was accomplished by pointwise laser scanning with a polarization-modulated optical

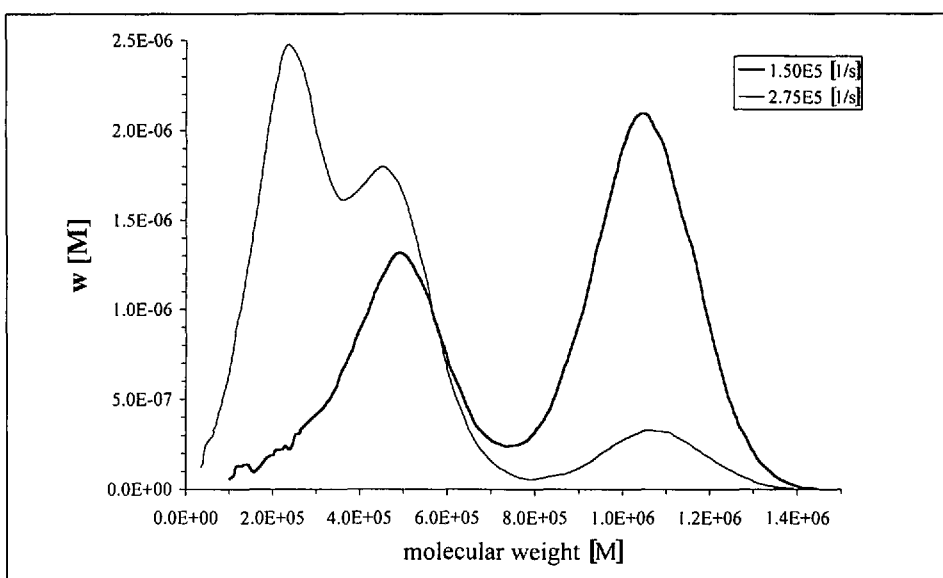


Fig. 2. Molecular weight distribution of a 5 ppm PS solution in decalin ($M_w = 1.03 \cdot 10^6$, $M_w/M_n = 1.017$), after a single passage through a narrow contraction, at the indicated strain-rates. A significant proportion of polymers have been degraded twice ($\sim M^0/4$) at the highest strain rate.

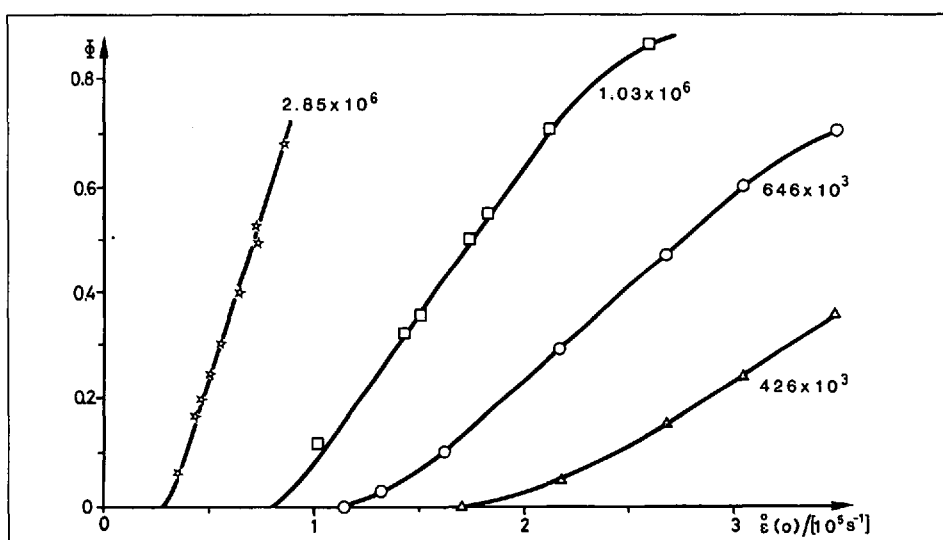


Fig. 3. Dependence of the degradation yield on strain-rate for different polymer molecular weights (values indicated on curves).

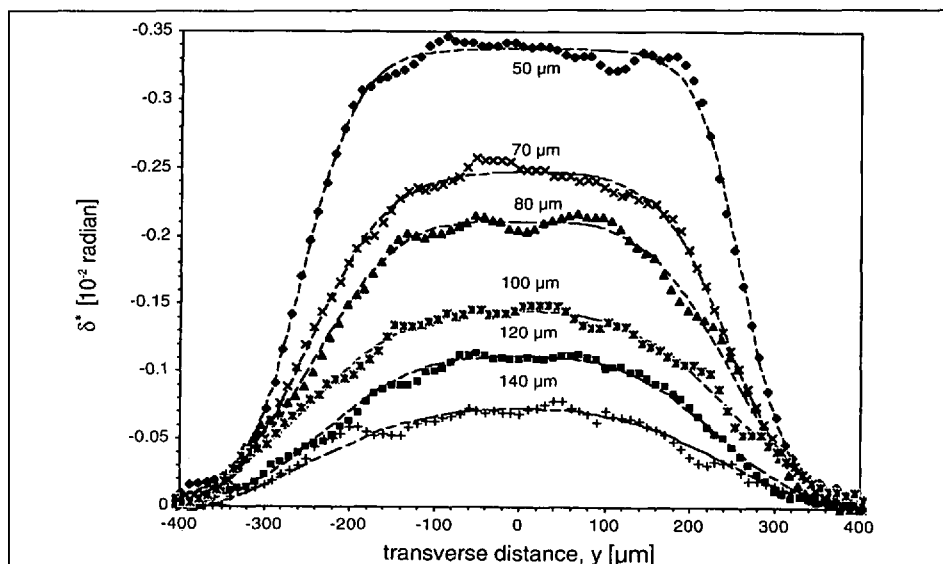


Fig. 4. Transverse retardation profiles for a 400 ppm $3.95 \cdot 10^6$ PS solution, scanned at the indicated distances from the inlet. Flow rate = $200 \text{ cm}^3/\text{min}$. Solid curves are fitted results from TableCurve™ 2D.

rheometer for increase sensitivity (Rheometrics, Piscataway, USA) [22].

Experimental data treatment is the second major source of difficulties. Flow birefringence in transmitted light gives only an effective (average) retardation δ^* and its transformation into birefringence $\Delta n(r)$, necessary for the determination of local polymer orientation, is highly involved in any 3-dimensional flow due to the variation of the principal axes of the refractive index tensor along the optical path of the probe beam [23]. For this reason, most birefringence measurements are restricted to slit or wedge flow. The few experiments which have been reported in axisymmetric flows [24] consider only an average value for the birefringence rather than its local distribution and are thus unsuitable for polymer dynamics studies. To the best of our knowledge, no attempt to convert experimental retardations into birefringence distributions has ever been reported before in axisymmetric flow. In the present study, the conversion of δ^* into $\Delta n(r)$ was performed by numerical Inverse Abel transform in combination with molecular orientation information obtained from flow field simulation (Fig. 5). The reader interested in the details of this technique can consult [25] (p.195 & 211).

The presence of maxima near the edges of the capillary entrance was the most noticeable feature of the radial birefringence distribution. Since the flow field is only purely extensional along the flow symmetry axis, it was anticipated that the propensity for polymer deformation should diminish rather than increase at the approach of the entrance lip, where shearing is predominant. Detailed flow field calculations provide a satisfactory explanation for this phenomenon: by proving the existence of extreme elongational strain-rates for streamlines closest to the orifice entrance lips ('re-entrant corner' effect). These transient strain rates can promote a high degree of chain orientation. Assuming that chains are deformed affinely with the surrounding fluid element above a critical strain-rate, the degree of chain orientation was calculated for the different streamlines, giving a peak birefringence near the orifice walls (Fig. 6).

Even if quantitative agreement between calculations and measurements is not expected in view of the crudeness of the affine deformation model, the calculated radial birefringence distributions reproduce remarkably well most of the experimental observations, *i.e.* the presence of maximum birefringence near the

entrance edges for short axial distances, and the relative increase of this maximum with polymer MW (not shown on Fig. 5).

The degree of orientation which can be achieved in decalin remains modest when compared to the maximum birefringence for fully oriented PS chains in solution ($\Delta n_{\max} = -1.35 \cdot 10^{-7}/\text{ppm}$). The use of a high MW sample dissolved in a

thermodynamically good solvent, such as 1-methyl-naphthalene, may increase the degree of molecular stretching. Axial birefringence distribution obtained with a $11.6 \cdot 10^6$ PS solution showed indeed that complete segmental orientation may be reached in this solvent at the highest flow rate (Fig. 7). Another striking feature of the birefringence distribution is the occurrence of multiple saturation plateaus,

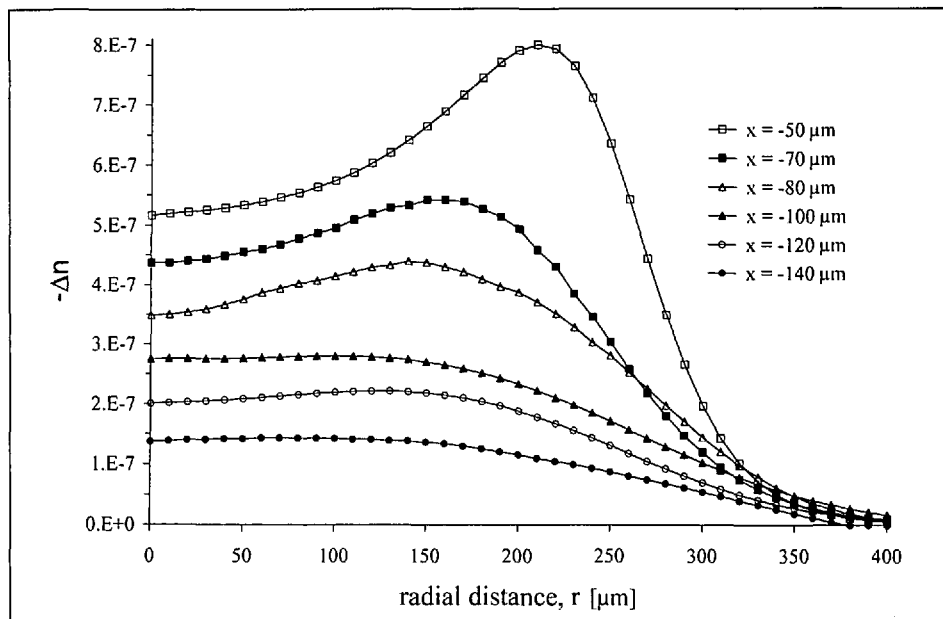


Fig. 5. Radial birefringence distribution, $\Delta n(r)$, calculated from the effective retardation data of Fig. 4 and the orientation of the first eigenvector of the rate of deformation tensor.

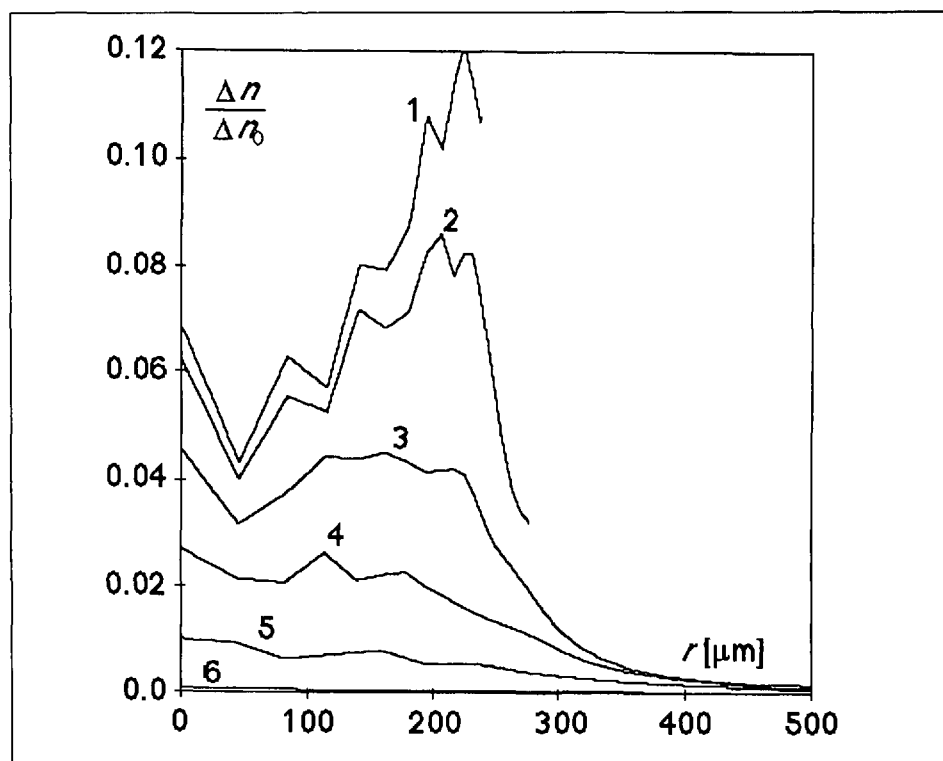


Fig. 6. Radial birefringence distributions calculated with the affine deformation model for a flow rate of $100 \text{ cm}^3/\text{min}$, at several distances x from the jet entrance. 1 : $x = -20 \mu\text{m}$, 2 : $x = -50 \mu\text{m}$, 3 : $x = -100 \mu\text{m}$, 4 : $x = -200 \mu\text{m}$, 5 : $x = -500 \mu\text{m}$. The peak in the birefringence distribution should be interpreted in light of the stress singularity at the re-entrant corner ([26]).

with value increasing with flow rate, at the approach of orifice entrance. The occurrence of well-defined birefringence plateaus at intermediate states of segmental orientation indicates the presence of transient conformations which are sufficiently rigid to resist further stretching by the velocity gradient, in a similar way to the 'frozen chains' suggested by James and coworkers [27] or the 'kinks dynamics' models of Larson [28] and Hinch [29].

2.3. Polarized Fluorescence

Owing to the relative simplicity of the equipment and the diversity of molecular information which can be obtained, birefringence has enjoyed a large central role in the study of polymer chain deformation in flow. The technique, however, can give only a mean degree of segmental orientation averaged over the whole molecule. It cannot, for instance, differentiate segmental orientation at the chain centre from orientation near the chain ends. To obtain local information on segmental dynamics, it is necessary to rely on spectroscopic techniques based on covalently bonded chemical markers which act as probes at selected positions along the macromolecule. In this investigation, fluorescence labelling was used to study the local uncoiling behaviour of PS chains at the stagnation point in an opposed-jet flow. Three high MW anthracene-labeled polymers were used: PS 'A' and 'B' are centre-labelled molecules synthesized by anionic coupling with dibromomethyl anthracene, with $M_w = 686 \cdot 10^3$, $M_w/M_n = 1.11$ and $M_w = 2.38 \cdot 10^6$, $M_w/M_n = 1.16$, respectively. Sample 'C' with $M_w = 1.23 \cdot 10^6$, $M_w/M_n = 1.25$ contains an anthracene group near one of the chain ends; it was obtained by flow-induced degradation after multiple recirculation of a dilute solution of PS 'B' across a narrow contraction.

Fluorescent depolarisation techniques have been used extensively to determine local orientation of bulk polymers [30], and molecular rotational motions either in polymer melts or in solutions [31]. In most of the investigations, the polymer is under quiescent conditions, being at rest or subjected solely to the Brownian motion of surrounding solvent. To the best of our knowledge, the fluorescence depolarisation technique has never been applied to polymer systems subjected to fast time-dependent perturbations such as in flowing dilute polymer solutions. Two practical difficulties, first in the synthesis of labelled polymer of sufficiently high MW, and secondly, in obtaining adequate

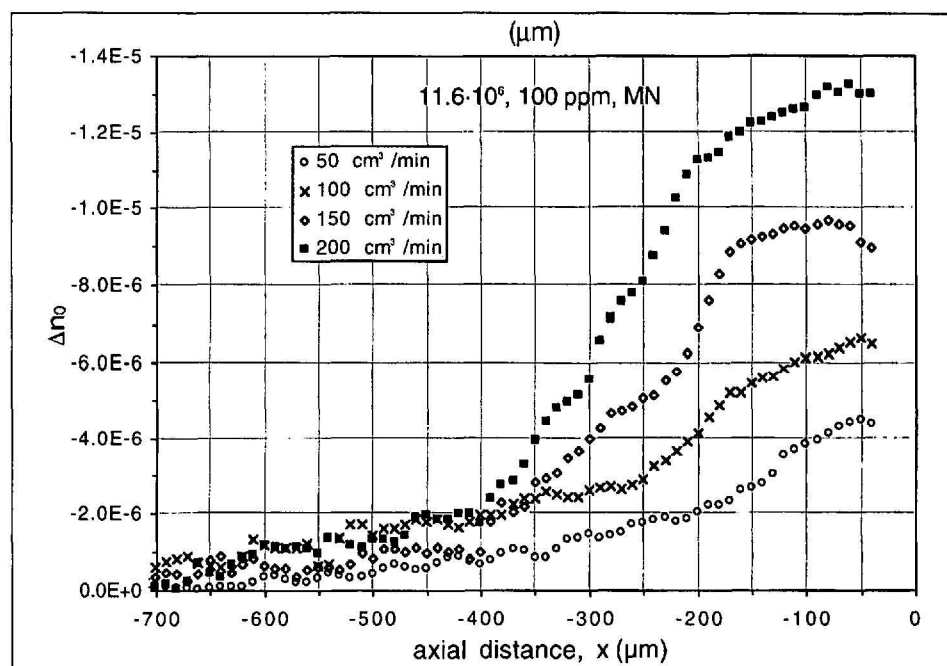


Fig. 7. Central local birefringence Δn_0 as a function of axial distance (x) for a 100 ppm $11.6 \cdot 10^6$ PS solution in 1-methyl-naphthalene, at the indicated flow rates. All results are corrected for solvent birefringence.

signal-to-noise ratio, may explain this delay in experimentation. In view of the low concentration of the chromophore groups, dictated by the high MW of the sample and the extreme dilution of the polymer to minimize chain interactions, a highly sensitive instrument must be selected. For this purpose, a novel rheo-fluorescence set-up based on an Argon laser operating in the UV at 362 nm and fast polarization-modulation technique has been developed in collaboration with Prof. G.G. Fuller from Stanford University (Fig. 8).

Owing to its versatility, Mueller matrix calculus has become an integral part of the design, data analysis and physical interpretation of polarimetry experiments. Analysis starts with the Stokes vector (S_0) of the incident light represented by a four-element column $[s_0, s_1, s_2, s_3]^T$ which describes the intensity and polarization state of the light beam. The output Stokes vector after an optical element is related to the input Stokes vector multiplied by the Mueller matrix corresponding to that component. According to this rule, the output Stokes vector following a train of optical elements numbered from 1 to M is simply given by a series of Mueller matrix multiplications:

$$S_M = M_M M_{M-1} \dots M_1 S_0 \quad (1)$$

After performing the matrix calculations, the intensity measured by the photomultiplier tube is determined to be:

$$I = I_{dc} + I_{\omega} \sin \omega t + I_{2\omega} \cos 2\omega t + \dots \quad (2)$$

$$\text{with } I_{dc} = (I_0/4) \cdot (M_{11} + M_{31}) \quad (3)$$

$$I_{\omega} = (I_0/4) \cdot 2J_1(A) (M_{14} + M_{34}) \sin \omega t \quad (4)$$

$$I_{2\omega} = (I_0/4) \cdot 2J_2(A) (M_{12} + M_{32}) \cos 2\omega t \quad (5)$$

M_{11} , M_{12} , etc. are elements of the Mueller matrix for the measured sample; J_1 and J_2 are Bessel function of first and second order, respectively, of the amplitude A of the photoelastic modulator [32].

For uniaxial stretching along the x direction, several elements of the sample Mueller matrix can be simplified, resulting in a first harmonic term which is function of fluorescence and sample birefringence, and a second harmonic term which depends only on the fluorescence tensor α_{ij} . By determining the ratio $I_{2\omega}/I_{dc}$ with a lock-in amplifier, it is possible to obtain the fluorescence anisotropy related to the second and fourth moment of the orientation distribution:

$$\begin{aligned} I_{2\omega}/I_{dc} &= 2 J_2(A) \cdot (M_{12} + M_{32}) / (M_{11} + M_{31}) \\ &= 2 J_2(A) \cdot \langle \alpha_{xx}^2 - \alpha_{yy}^2 \rangle / \langle \alpha_{xx}^2 + \alpha_{yy}^2 + 2 \alpha_{xy}^2 \rangle \end{aligned} \quad (6)$$

Experimental data obtained with the three anthracene-labeled polymers, PS 'A', PS 'B' and PS 'C', are given in Fig. 9. As expected, orientation of the chain centre occurred at higher strain rate with decreasing MW (as a result of de-

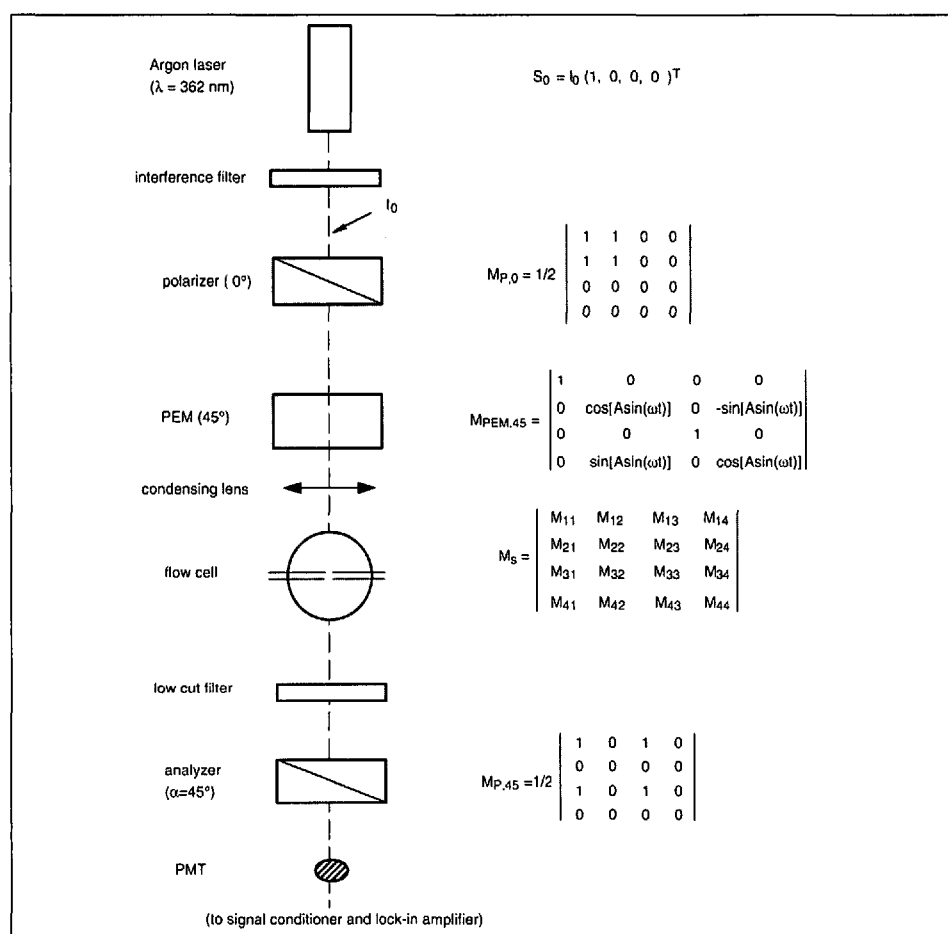


Fig. 8. Optical arrangement for polarization-modulated fluorescence spectroscopy with the associated Mueller matrices elements. Note that the detector is in-line with the incoming beam: this geometry has the advantage of giving a signal above a zero baseline resulting in a better S/N ratio in comparison to the conventional 90° configuration.

creasing molecular relaxation time), while orientation near the chain ends is practically non-existent at any strain-rate. Superposition of the fluorescence curve with the birefringence data obtained under identical experimental con-

ditions reveals, however, the surprising result that the polymer centre positioned itself with the velocity gradient even more gradually than the average segmental orientation (Fig. 10) [33]. This observation could not be explained by any cur-

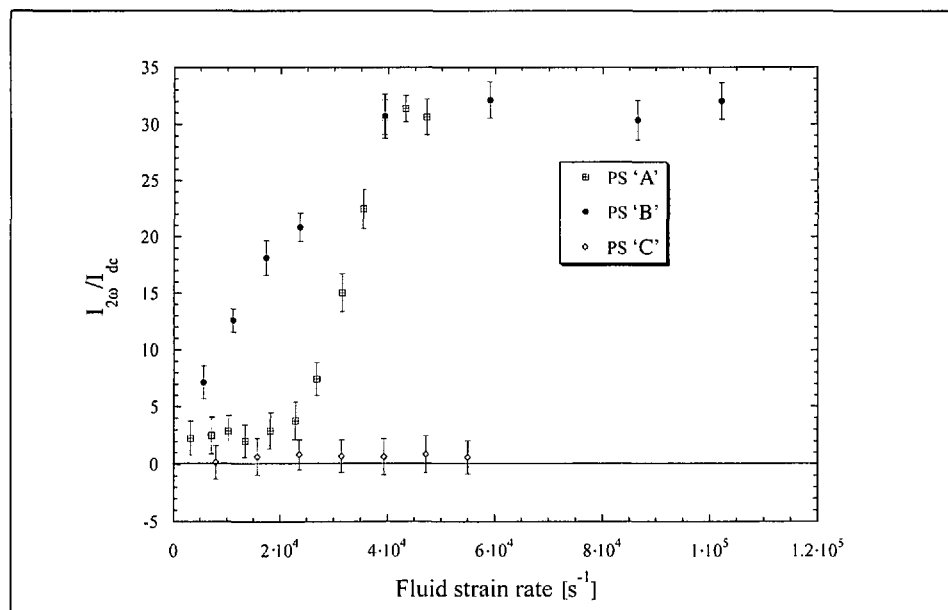


Fig. 9. Dependence of the depolarisation ratio ($I_{2\omega}/I_{dc}$) on fluid strain rate for different anthracene-labeled PS (solvent: bis(2-ethylhexyl) phthalate at 22°C , concentration: 100 ppm). The error bars are standard deviation over 100 measurements.

rent model of polymer dynamics. The 'yo-yo' model, for instance, predicts that the chain centre should align with the flow field well before the rest of the polymer [34]. The kink model predicts a much weaker dependence of segmental orientation on chain position [28][29].

Recent studies by the Stanford group on individual motion of DNA molecules reveal that identical polymers in identical conditions can uncoil quite differently in an elongational flow following small random thermal fluctuations which get magnified into dramatic differences during the course of deformation [35]. It is our belief that the perplexing result observed in fluorescence depolarisation experiments, probed over a large collection of molecules, could be explained only once the observed 'molecular individualism' is properly taken into account.

2.4. Single-Chain Visualization

Rheo-optical spectroscopy has now reached the stage in which relaxation processes of particular molecules in a multi-component system, or of specific parts of a molecule in a topologically complex polymer can be selectively probed. Even at this high level of precision, rheo-optical instruments can determine only properties which has been averaged over a population of 10^7 to 10^9 molecules. Ideally, the best means to determine dynamics properties would be by direct time-resolved observation of individual macromolecular motion. Such a prospect existed for DNA strands which, after being marked with a suitable chromophore, could be visualized by epifluorescence microscopy [35]. Similar experiments have been repeated in our laboratory with λ -phage DNA molecules decorated with the fluorescent dye YOYO-1 (Fig. 11).

DNA molecules are rather rigid (worm-like chain) and direct visualization of PS chains marked with fluorescent chromophores may be more representative of flexible synthetic polymers. Several material and technical challenges must be solved, however, before performing this experiment. First, the optimum contour length of the macromolecule to be visualized must be of the order of $20 \mu\text{m}$, to be within the depth of focus of the microscope objective. For a typical synthetic polymer such as PS, this size is equivalent to a MW of $10 \cdot 10^6$. Secondly, polymer dynamics are highly dependent on chain length. To differentiate dimensional from conformational factors, monosized or at least very low polydispersity

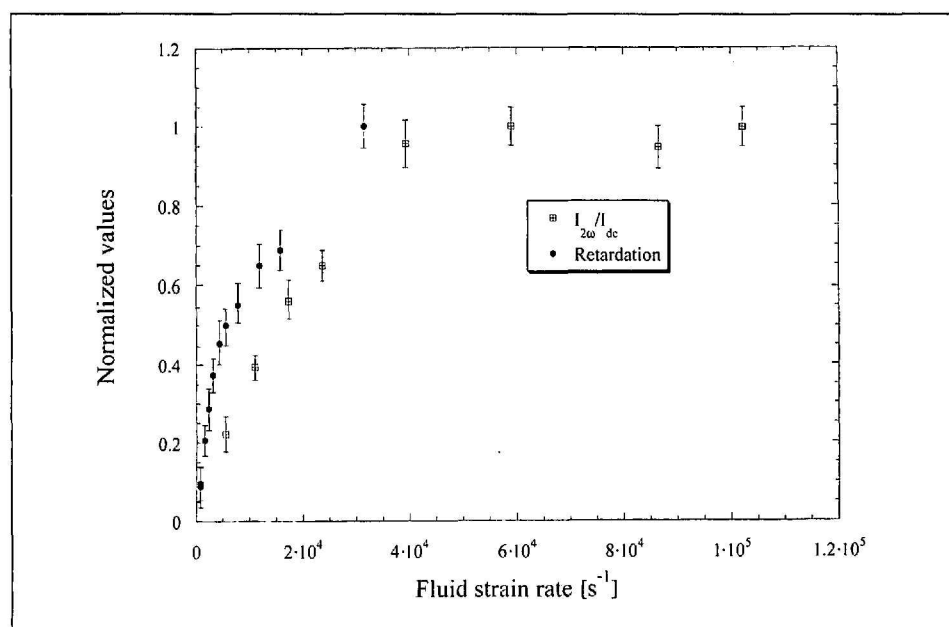


Fig. 10. Superposition of the depolarisation ratio ($I_{2\omega}/I_{dc}$) and the birefringence curve for the $2.38 \cdot 10^6$ centre-labelled PS (same experimental conditions as in Fig. 9).

polymers are required. In addition, the number of grafted fluorescent groups per molecule should be sufficient for the emitted light to be detected by the iCCD (typically $\sim 15\%$ for a $10 \cdot 10^6$ PS).

To overcome inherent difficulties of anionic polymerisation in the ultra-high MW range, we explored in this study the possibility of obtaining fluorescent macromolecules from commercially available PS standards. Owing to the presence of aromatic rings, PS can undergo a multitude of reactions with low molar mass compounds. After multiple experimentation, we found that potassium superbase metallation is one of the rare techniques capable of functionalising the polymer without altering the main chain backbone (Scheme) [36].

Side reactions such as chain coupling and bond scission can be limited by working in THF at -75°C . Gel permeation chromatography combined with on-line viscometric, refractive index and fluorescence detection, allows us to verify that degradation did not exceed 1 bond scission/180 000 monomer units. Although this value is reasonably low for conventional polymer samples, it represents nevertheless a degradation yield of over 50% when transposed to a $10 \cdot 10^6$ MW polymer (Fig. 12). Another encountered difficulty is the low degree of grafting which can be achieved even after extended reaction time at cryogenic temperature (4.5% for a 10^6 MW sample and $< 2\%$ for a $11.6 \cdot 10^6$ after 7 h of reaction). Increasing the degree of grafting while keeping degradation below the current value are two contradictory requirements which will need special considerations in our future investigations [37].

3. Prospects and Conclusions

In a series of projects dedicated to flexible chain dynamics in elongational flow, we have developed the capability to monitor experimentally the deformation of isolated polymer molecules in

strong flow up to the point of fracture. Results from a combination of different analytical techniques allow us to confirm the importance of non-equilibrium conformations during rapid deformation of molecular coils in 'strong' flow. Although steady-state conformations of flexible polymer chains in elongational flow seem now to be well-understood, the kinetics of the transition from the coiled to the extended state remain essentially a matter for conjecture. Most of the problems associated with the limited residence time in the strong flow region and the lifetime of metastable states were formulated by researchers more than ten years ago [16][28][29]. However, the importance of 'conformational polydispersity' [38] in flow which is thought to be 'quasi-steady' was rarely addressed. Recent single DNA chain observation by the group of Prof. Chu at Stanford University demonstrates that some non-equilibrium conformations may persist for time much longer than the experimental observation duration even for molecules trapped at the stagnation point in cross-slot flow. In addition, individual motion of DNA molecules revealed that identical polymers in identical conditions can uncoil quite differently in an elongational

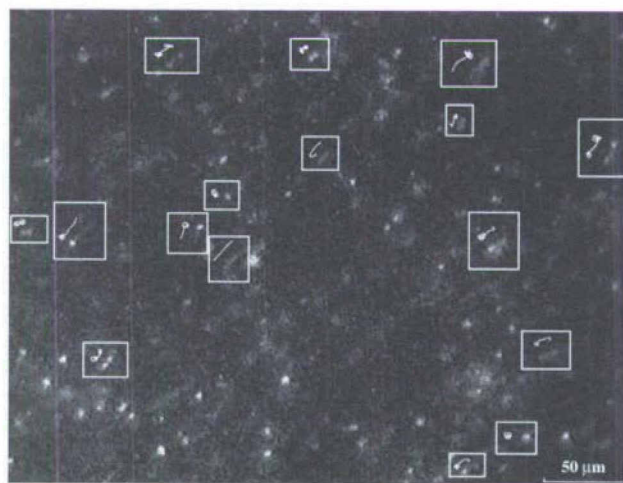
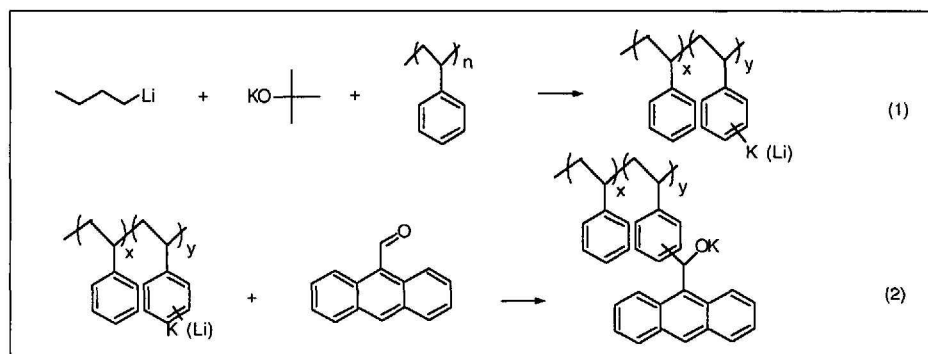


Fig. 11. Fluorescence microphotography of λ -DNA molecules decorated with YOYO-1 and sheared between two glass plates. Different conformations, present in the figure, are redrawn in white next to the original tracings for better visualization.



Scheme. Introduction of anthracene onto PS by potassium superbase metallation followed by electrophilic substitution with anthracene-9-carbaldehyde.

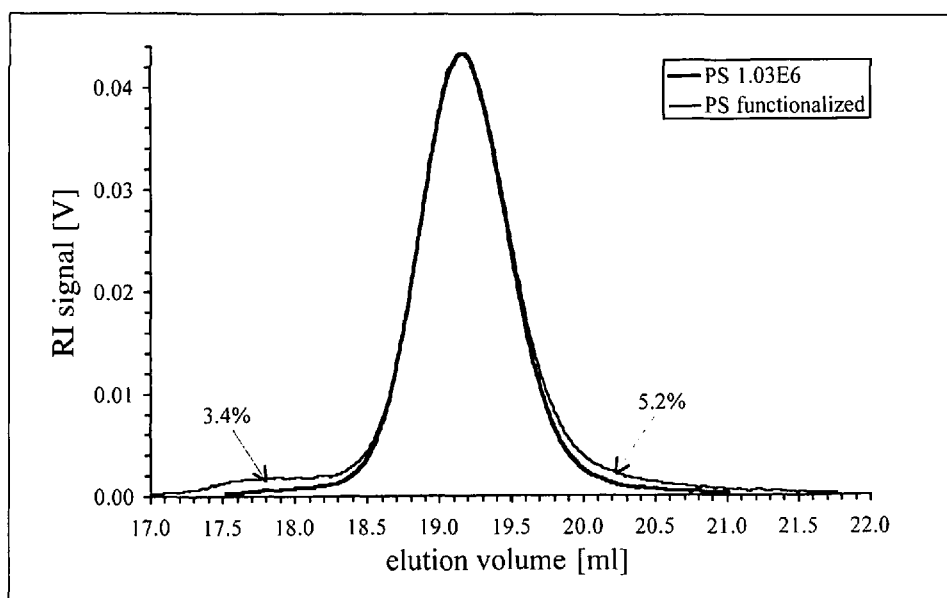


Fig. 12. Overlay of the GPC tracings normalized to the maximum of RI signals, for a $1.03 \cdot 10^6$ PS before and after functionalisation with 4.5% anthracene. The indicated arrows correspond to the fractions of degraded polymer.

flow. As a result of this unpredictable behaviour, a 'mean-field' theory which was developed to fit experimental data probed over a large collection of molecules is unsuitable to infer molecular dynamics in 'strong' flow. Because present instrumentation can provide only information on the collective behaviour of macromolecules, models are needed to infer behaviour of individual molecules. Such models invariably rely on assumptions of questionable validity. Uncertainties in the field of polymer dynamics will persist as long as some breakthrough technique capable of discerning individual macromolecules is not developed. Based on the recent developments on single chain visualization and the technique of fluorophore labelling, it seems that the field of polymer characterization has now reached the stage at which direct study of single synthetic macromolecule motion may become a feasible reality.

Acknowledgements

The author gratefully acknowledge the assistance of Dr. C.J.G. Plummer in re-reading the manuscript, Dr. B. Debbaut for providing data for Fig. 6 and the Swiss National Science Foundation for continuing financial support of the project.

Received: January 15, 2001

- [1] a) A. Peterlin, *Pure Appl. Chem.* **1966**, *12*, 563; b) L.G. Leal, in 'Polymer-Flow Interaction', Ed.: Y. Rabin, American Institute of Physics, New York, **1985**, p.5.
- [2] T.Q. Nguyen, H.H. Kausch, *Adv. Polym. Sci.* **1992**, *100*, 75.
- [3] M.S. Jhon, G. Sekhon, R. Armstrong, *Adv. Chem. Phys.* **1993**, *66*, 153.
- [4] T.Q. Nguyen, Q.Z. Liang, H.H. Kausch, *Polymer* **1997**, *38*, 3783.
- [5] H. Staudinger, *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 3152.
- [6] T.Q. Nguyen, H.H. Kausch, *Chimia* **1986**, *40*, 129.
- [7] A. Keller, J.A. Odell, *Coll. & Polym. Sci.* **1985**, *263*, 181.
- [8] a) E.W. Merrill, P. Leopairat, *Polym. Eng. Sci.* **1980**, *20*, 505; b) A.F. Horn, E.W. Merrill, *Nature* **1984**, *312*, 140.
- [9] S.P. Carrington, J.A. Odell, *J. Non-Newtonian Fluid Mech.* **1996**, *67*, 269, and references therein.
- [10] J. Frenkel, *Acta Physicochim. URSS* **1944**, *19*, 51.
- [11] T.Q. Nguyen, H.H. Kausch, *Macromolecules* **1990**, *23*, 5137.
- [12] T.Q. Nguyen, H.H. Kausch, *Coll. & Polym. Sci.* **1986**, *264*, 764.
- [13] T.Q. Nguyen, H.H. Kausch, *Coll. & Polym. Sci.* **1991**, *269*, 1099.
- [14] T.Q. Nguyen, H.H. Kausch, *J. Non-Newtonian Fluid Mech.* **1988**, *30*, 125.
- [15] V. Zysman, T.Q. Nguyen, H.H. Kausch, *J. Polym. Sci. Polym. Phys.* **1994**, *32*, 1257.
- [16] Y. Rabin, *J. Non-Newtonian Fluid Mech.* **1988**, *30*, 119.
- [17] D.P. Pope, A. Keller, *Coll. & Polym. Sci.* **1977**, *255*, 633.
- [18] G.G. Fuller, L.G. Leal, *Rheol. Acta.* **1980**, *19*, 580.
- [19] O. Srivener, C. Berner, R. Cressely, R. Hocquart, R. Sellin, N.S. Vlachos, *J. Non-Newtonian Fluid Mech.* **1979**, *5*, 475.
- [20] T.Q. Nguyen, G. Yu, H.H. Kausch, *Macromolecules* **1995**, *28*, 4851.
- [21] a) D. Hunkeler, T.Q. Nguyen, H.H. Kausch, *Polymer* **1996**, *37*, 4257; b) *Polymer* **1996**, *37*, 4270.
- [22] a) G. Yu, 'Experimental investigation of single chain dynamics in elongational flow', Ph.D. thesis EPFL No.1523, **1996**; b) G. Yu, T.Q. Nguyen, H.H. Kausch, *J. Polym. Sci. Part B Polym. Phys.* **1998**, *36*, 1483.
- [23] a) S.R. Galante, P.L. Frattini, *J. Non-Newtonian Fluid Mech.* **1993**, *47*, 289; b) J.-M. Li and W. R. Burghardt, *J. Rheol.* **1995**, *39*, 743.
- [24] a) G.D. Eisenbrand, J.D. Goddard, *J. Non-Newtonian Fluid Mech.* **1982**, *11*, 337; b) H. Baaijens, 'Evaluation of Constitutive Equations for Polymer Melts and Solutions in Complex Flows', Ph.D. thesis, Eindhoven University of Technology, **1994**; c) J.-M. Li, W.R. Burghardt, *J. Rheol.* **1995**, *39*, 743.
- [25] T.Q. Nguyen, R. Porouchani, H.H. Kausch, in 'Flexible Chain Dynamics in Elongational Flow', Eds. T.Q. Nguyen, H.H. Kausch, Springer-Verlag, Berlin, Heidelberg, **1999**, p.185.
- [26] H.K. Moffat, *J. Fluid. Mech.* **1964**, *18*, 1.
- [27] a) D.F. James, J.H. Saringer, *J. Fluid Mech.* **1980**, *97*, 655; b) D.H. King, D.F. James, *J. Chem. Phys.* **1983**, *78*, 4749.
- [28] a) R.G. Larson, J.J. Magda, *Macromolecules* **1989**, *22*, 3004; b) R.G. Larson, *Rheol. Acta* **1990**, *29*, 371.
- [29] a) J.M. Rallison, E.J. Hinch, *J. Non-Newtonian Fluid Mech.* **1988**, *37*, 29; b) E.J. Hinch, *J. Non-Newtonian Fluid Mech.* **1994**, *54*, 209.
- [30] Y. Nishijima, Y. Onogi, T. Asai, *J. Polym. Sci. C* **1966**, *15*, 237.
- [31] J.-L. Viovy, L. Monnerie, *Adv. Polym. Sci.* **1985**, *67*, 99.
- [32] G.G. Fuller, 'Optical Rheometry of Complex Fluids', Oxford University Press, New York, **1995**, chapter 2.
- [33] P. Vurpillot, 'Dynamique des chaînes macromoléculaires en écoulement élongationnel par dépoliarisation de fluorescence', Ph.D. thesis EPFL No.1647, **1997**; b) T.Q. Nguyen, P. Vurpillot, H.H. Kausch, *Bull. Amer. Phys. Soc.* **1998**, *43*(1), 936.
- [34] G. Ryskin, *J. Fluid Mech.* **1987**, *178*, 423.
- [35] a) T.T. Perkins, D. Smith, S. Chu, *Science* **1997**, *276*, 2016; b) T.T. Perkins, D.E. Smith, S. Chu, in 'Flexible Polymer Chain Dynamics: theory and experiment', Eds. T.Q. Nguyen, H.H. Kausch, Springer-Verlag, Heidelberg, **1999**, p.283.
- [36] L. Lochmann, J.J. Fréchet, *Macromolecules* **1996**, *29*, 1767.
- [37] a) R. Porouchani, 'Biréfringence et visualisation de chaînes de Polystyrène isolées en écoulement élongationnel', thèse EPFL No. 2151, **2000**; b) R. Porouchani, L. Garamszegi, T.Q. Nguyen, J. Hilborn, *Macromol. Rapid Comm.* **2000**, *21*, 837.
- [38] V.N. Tsvetkov, 'Rigid-chain polymers: hydrodynamic and optical properties in solution', (transl. from Russian by E. A. Korolyova), Consultants Bureau, New York (etc.), **1989**, p.289.