

According to our opinion, this difference in the importance of the binding site phenomenon affords the main contribution to the observed behaviour of the two samples. Nevertheless, we cannot completely rule out the possible influence of compositional heterogeneity which may be expected to be much more important in the radical copolymer (high conversion) than in the hydrolysed sample (auto-retarded kinetics lead to very low composition fluctuations¹⁵).

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Laser light scattering characterization of rod-like polymers in corrosive solvents: Kevlar in concentrated sulphuric acid

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In this communication, we report the preliminary results of a study on the molecular characterization of poly(1,4-phenyleneterephthalamide) (PPTA), Kevlar, in concentrated sulphuric acid. By combining static and dynamic light scattering measurements, we were able to determine directly for the first time, the molecular weight distribution of PPTA. The laser light scattering technique offers a new complementary analytical approach to size exclusion chromatography, which is difficult to perform for polymer solutions in corrosive solvents.

(Keywords: laser light scattering; characterization; rod-like polymers; Kevlar)

Poly(1,4-phenyleneterephthalamide) (PPTA), Kevlar, fibres have high tenacity and modulus. The material often forms an important component in polymer composites. However, characterization of *para*-aromatic polyamides has been a difficult task. In particular, PPTA is soluble mainly in corrosive strong protic (sulphonic) acids, such as methane sulphonic acid, chlorosulphonic acid and concentrated sulphuric acid, whose corrosive properties require special modifications on analytical instrumentation related to size exclusion chromatography. Therefore, although PPTA was prepared years ago and Kevlar fibres have found many unique applications, no absolute method for molecular characterization, i.e., molecular weight distribution, of PPTA exists. In this communication, we want to report the first direct determination of the molecular weight distribution of PPTA. The details will be described in two subsequent articles on (1) static and dynamic properties of dilute solutions of PPTA in

concentrated sulphuric acid and (2) determination of molecular weight distribution. It is sufficient for us to outline here our approach to the problem and to emphasize the general features strongly suggesting that laser light scattering can be established as a powerful analytical method which complements size exclusion chromatography, and in the case of rod-like polymers such as PPTA, is the only 'direct' technique in practice.

Solution properties of PPTA have been investigated by Berry and his coworkers^{1,2}. In his pioneering and extensive studies¹⁻⁶, Berry has solved many of the experimental difficulties associated with PPTA solutions. For examples, PPTA was shown to be prone to interchain aggregation and to have a rod-like conformation with a persistence length of at least 50 nm in chlorosulphonic acid. We have taken advantage of his experience and considered specific procedures in order to overcome both experimental and theoretical complications. These include (1) absorption of light by the reddish-tinted PPTA solution in the visible range, (2) strong fluorescence of PPTA in concentrated sulphuric acid at an incident

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wavelength λ_0 of 488 nm, (3) considerable protonation of PPTA in concentrated sulphuric acid resulting in the formation of macro-ions, (4) interchain interactions including aggregation, (5) clarification of PPTA solutions, (6) the use of mixed solvents, and (7) optical anisotropy of PPTA requiring analysis of vertical and horizontal components R_{Vv} and R_{Hv} of the Rayleigh ratio using vertically polarized incident light based on rod-like chains⁷⁻¹⁰.

In our experiments, five different molecular weight samples of PPTA were synthesized by polycondensation of terephthaloyl chloride and *p*-phenylene diamine at the Institute of Chemistry in Beijing, using known procedures¹¹. Solutions of known PPTA concentration in 96% sulphuric acid and 0.1 N K_2SO_4 were individually prepared, centrifuged at $\sim 10K$ gravity for one to three hours in order to remove dust and sealed in 10 mm o.d. cylindrical light scattering cells. The light scattering spectrometer¹² has been modified to include a Glan-laser prism as a polarizer and a Glan-Taylor prism as an analyser. We used a Lexel model 92 argon ion laser operating at $\lambda_0 = 488$ nm and 100–250 mW. The solutions were again centrifuged for at least 1 h at $\sim 10K$ gravity immediately prior to light scattering measurements at 30°C.

From the scattered intensity data, we were able to determine the radius of gyration R_g , the second virial coefficient A_2 and the weight average molecular weight M_w . From time correlation function data, we were able to successfully perform a correlation function profile analysis¹³ using the singular value decomposition technique¹⁴.

The measured single-clipped photoelectron count autocorrelation function for a detector of finite effective photocathode has the form

$$G_k^{(2)}(\tau) = N_s \langle n_k \rangle \langle n \rangle (1 + \beta |g^{(1)}(\tau)|^2) \quad (1)$$

where $g^{(1)}(\tau)$ is the first-order normalized correlation function of the scattered electric field, k is the clipping level, τ is the delay time, $\langle n_k \rangle$ and $\langle n \rangle$ are the mean clipped and unclipped counts per sample time, and N_s is the total number of samples with the baseline $A = N_s \langle n_k \rangle \langle n \rangle$. β is a spatial coherence factor and is usually taken as an unknown parameter in the data fitting procedure. For PPTA solutions, it is important to realize that the scaling exponent α_D , defined by

$$D = k_D M^{-\alpha_D}, \quad (2)$$

is likely to be of the order of 0.75 because of the rod-like nature of PPTA in solvents, such as concentrated sulphuric acid; where D and M are, respectively, the translational diffusion coefficient at infinite dilution and the molecular weight; and k_D is a proportionality constant. For a solution of polydisperse macromolecules in solution, we are interested in retrieving the normalized characteristic linewidth distribution function $G(\Gamma)$ from the electric field time correlation function $|g^{(1)}(\tau)|$:

$$g^{(1)}(K, \tau) = \int_0^\infty G(K, \Gamma) e^{-\Gamma(K)\tau} d\Gamma \quad (3)$$

where $K \equiv (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of momentum transfer vector. It should be recognized that $g^{(1)}(K, \tau)$ is bandwidth limited and contains noise. Furthermore, in

the Laplace transform, we have a finite support ratio $\gamma \equiv \Gamma_{\max}/\Gamma_{\min}$, where Γ_{\max} and Γ_{\min} are the upper and lower frequencies of the characteristic linewidth distribution $G(K, \Gamma)$. Therefore, correlation function profile analysis represents a contiguous part of our experiments. In our iterative approach, we were concerned with not only the baseline but also the range and location of delay time^{13,15}. For rod-like molecules such as PPTA, clarification of solution becomes one of the experimental difficulties which requires special attention. Furthermore, according to equation (2), the larger α_D value (> 0.6) broadens the characteristic linewidth distribution of the same molecular weight distribution when the polymer molecules become more rigid, i.e., when α_D becomes larger. Therefore, we need to pay closer attention to the range and location of delay time used to see whether the limited bandwidth of the measured time correlation function has covered properly the characteristic linewidth distribution under investigation.

Equation (3) is a Fredholm integral equation of the first kind with a Laplace kernel which, in the presence of noise, leads to the notoriously ill-conditioned inversion problem. The amount of information that can be recovered about $G(\Gamma)$ is limited. However, in the determination of molecular weight distribution, Γ_{\max} and Γ_{\min} are limited by physical constraints and the form of $G(\Gamma)$ can generally be represented by well-behaved distributions. Therefore, by stating the problem in terms of a large number of information elements and by applying a rank reduction technique midway through the solution, we can retain a maximum number of independent elements. In the multiexponential approach, we model $G(\Gamma)$ as

$$G(\Gamma) = \sum_{i=1}^N I_i \delta(\Gamma - \Gamma_i) \quad (4)$$

giving $|g^{(1)}(\tau)| = \sum_{i=1}^N I_i e^{-\Gamma_i \tau}$ where we fix the Γ_i values and fit values of I_i . At infinite dilution and in the limit of small K where the particle scattering factor $P(KR_g) \approx 1$, $\Gamma_i = D_i K^2$, and $I_i = N_i M_i^2$. So, we see that in a light-scattering characterization of molecular weight distribution of polymers in solution the number has been weighted by M^2 . In practice, we need also to take into account the concentration effect as well as the interference effect which is usually appreciable for rod-like polymers in solution.

All of the above complications, including problems related to rod-like polymers, the iterative approach to laser light scattering, the ill-conditioned nature of inverting the Laplace transform, and effects of particle interference and interactions, have been considered and resolved. Figure 1 shows a molecular weight distribution of PPTA with $M_z:M_w:M_n = > 4.5 : > 1.6 : 1$ illustrating the success of this new analytical method. We have noted that $M_w/M_n \geq 1.8$ is somewhat less than the Flory-Schulz most probable distribution for polycondensation polymers. Final completion of experiments and analysis is in progress.

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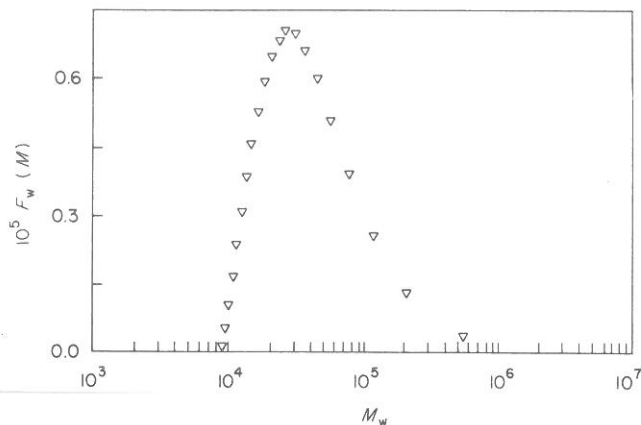


Figure 1 Plot of (unnormalized) weight fraction F_w of PPTA as a function of molecular weight M_w

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The determination of $d \ln \bar{r}_0^2 / dT$ by the method of temperature induced creep

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It is shown by the method of temperature induced creep that the traditional solution to the hysteresis problem in the classical thermoelastic experiment on elastomers is erroneous. Errors arise in the determined coefficient $f^{-1}(\partial f / \partial T)_{PL}$ because the observed f exceeds the equilibrium value and because $(\partial f / \partial T)_{PL}$ obtained on rapid cooling and heating is less than the equilibrium value: when forming the product $f^{-1}(\partial f / \partial T)_{PL}$ the two errors are cumulative. In the new method of temperature induced creep it is assumed *a priori* that equilibrium under a constant stress is never obtained: with this realistic premise values of $d \ln \bar{r}_0^2 / dT$ and f_e / f may be obtained with good precision.

(Keywords: elastomer; thermoelastic; \bar{r}_0^2 ; f_e / f ; temperature induced creep)

In this communication we outline a new method for determining the temperature dependence of \bar{r}_0^2 , the mean square end-to-end vector length of a macromolecule,

$$\kappa = \frac{d \ln \bar{r}_0^2}{dT} \quad (1)$$

This quantity is of theoretical molecular significance and in the theory of rubber elasticity controls the ratio of the energetic to the total retractive force¹⁻⁴. At temperature T this ratio is given by

$$(f_e / f) = T \kappa \quad (2)$$

The new method is not subject to the several systematic errors which occur in the classical thermo-elastic experiment⁵, of which the most formidable is that due to hysteresis⁶, a failure of the elastomer to attain mechanical

equilibrium within the limited time scale of the experiment.

The traditional method of eliminating the hysteresis perturbation was first described by Joule⁷. All later developments (whether in creep experiments — comparable to those of Joule — or in stress relaxation) have been based on the same principle. It is probably worth quoting at some length from Flory's⁶ description of the experimental procedure.

'Hysteresis in the stress-strain behaviour of rubber and rubberlike materials has presented the most serious problem encountered in the execution of otherwise simple experiments on the change of stress in stretched rubber with temperature at constant length or at constant elongation. The stress exerted by the sample held at fixed length decays with time towards a limiting value, but the rate of approach to this limit decreases with time in such a way as virtually to preclude attainment of the actual limiting stress within any