Table 3 Precipitation ranges for 1% w/w solutions of alternating block polymers and the preformed alternating copolymers

Polymer	Solvent	Precipitant	Precipitation range Volume ratio : precipitant/solvent
Poly(St-alt-MA)	MEK	methanol	1.3–2.2
Polymer (VIII)	MEK	methanol	0.7–1.1 (0.9)*
Polymer (IX)	MEK	methanol	0.9–1.2 (1.1)
Poly(Ip-alt-MA)	toluene	cyclohexane	no precipitation
Polymer (X)	toluene	cyclohexane	1.2–2.0 (1.8)
Poly(Bd-alt-MA)	toluene	cyclohexane	no precipitation
Polymer (XI)	toluene	cyclohexane	1.1–2.0 (1.8)

* Used for separating block polymer

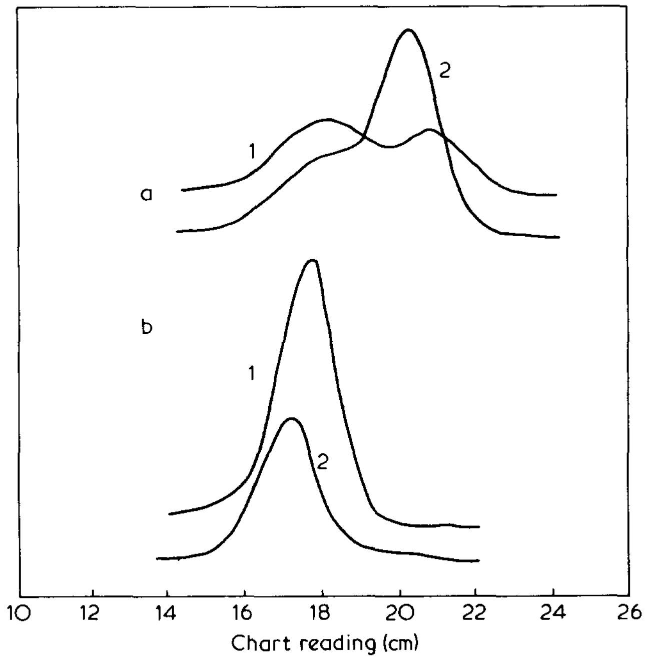

Figure 2 Purification of block polymer (VIII) by fractionation. G.p.c. traces: (a), unfractionated; (b), fractionated sample. Detection: 1 refractometer, 2 u.v. spectrophotometer (λ = 260 nm)

preformed alternating copolymers are set out in *Table 3*. The efficiency of the fractionation procedure is illustrated by the g.p.c. data in *Figure 2*. Similar results were obtained with all the polymers (VIII)–(XI).

The n.m.r. spectra of the block polymers (in $CDCl_3$ solution) were completely consistent with fully-alternating structures and permitted estimates to be made of the ratios of different types of unit in the polymers, notably St/Ip and St/Bd (*Table 2*). Since molecular weights of the preformed copolymers are known (*Table 1*), the molecular weights of the final polymers can be calculated with the aid of these ratios. Results are given in *Table 2*, from which it will be seen that reasonable agreement between calculated and observed osmometric values are obtained if the polymers have three-block structures (VIII)–(XI). Thus termination by radical combination (1d) must occur. The presence of two-block polymers would imply termination by disproportionation (1c) and/or chain transfer to preformed polymer in the second polymerization[6]. We conclude that either the fractionation removed any two-block polymers, or the two processes mentioned do not occur significantly.

We hope to report on the properties of these novel polymers subsequently.

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Potential artefacts in the determination of the optical anisotropy of macromolecules by light scattering

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A pronounced optical anisotropy of polymers in solution is a relatively rare phenomenon. The classical paper by Utiyama and Kurata[1] presents a detailed theoretical analysis of this phenomenon. A considerable optical anisotropy reflected in the high depolarization of scattered light was found experimentally by Utiyama with several (and with one in particular) fractions of isotactic polystyrene in chlorobenzene[2]. Reiss[3] observed the effect of optical anisotropy in light scattering measurements of solutions of atactic polystyrene in bromoform; the anisotropic character of the samples became less pronounced with increasing temperature. A similar trend in the change of optical anisotropy has been found by Utiyama and Tsunashima[4] for poly(α-methylstyrene) in *trans*-decalin. Carpenter *et al.*[5] have described marked anisotropic behaviour of filtered polyoxyethylene solutions in dioxan, in contrast with unfiltered solutions, where the optical anisotropy was negligible.

When studying light scattering from solutions of poly(methyl methacrylate) of various tacticities in butyl acetate, we also observed in several cases a pronounced depolarization of light incident on the photomultiplier, reflected among other things in typical concave angular dependences[1,2,5] of Kc/R_θ on $\sin^2(\theta/2)$ (*Figure 1*). However, in most solutions this effect has not been observed. The insertion of an antifluorescence filter did

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not affect the character of scattered light. We therefore ruled out the possibility of fluorescence and saw a logical explanation in the optical anisotropy of scattering macromolecules. It appeared later that our case concerned an experimental artefact caused by partial passage of the primary beam through the meniscus of the solution. By elevation of the cell containing solution in the apparatus so as to let the whole beam pass through solution only, the depolarization of scattered light has disappeared (*Figure 1*). When the primary beam passes through the meniscus of the solution, a complicated refraction and reflection obviously take place, and part of the unpolarized stray light hits the detector. With rising temperature, we also observed a decrease in apparent anisotropy; due to the thermal expansion of solution, the meniscus moves from the space irradiated with the primary beam.

One of the versions of correction for the optical anisotropy of solutions suggested by Utiyama and Kurata[1] may be written in the form

$$R_\theta^+(V,v)=R_\theta(V,v)-C \qquad (1)$$

where

$$C=\frac{4}{3}R_{90}(H,h) \qquad (2)$$

C is the correction factor for optical anisotropy proportional to the parameter of optical anisotropy, δ. For unpolarized light, the relation

$$R_\theta^+(U,u)=\frac{1+\cos^2\theta}{2}R_\theta^+(V,v) \qquad (3)$$

holds. R_θ, R_θ^+ are the experimental and corrected Rayleigh ratios for scattered light observed at the angle θ determined with unpolarized (U,u), and with vertically (V,v) and horizontally (H,h) polarized light (capital letters are related to the polarization of scattered light, small letters denote the polarization of the primary beam).

By neglecting its proper physical meaning, the correction of this type may often be mechanically, and with fairly good result, used also in the case where the depolarization of scattered light has causes other than the optical anisotropy of scattering macromolecules. If C is regarded as an adjustable parameter, it is possible, e.g. to correct the depolarization due to the reflection of the primary beam from the solution surface (*Figure 1*, C taken as $(2/3)R_{90}(H,h)$). It can also be demonstrated that the depolarization contribution due to fluorescence may be eliminated by putting $C=R_{90}(H,h)$. If the intensity of fluorescence does not exceed 15–20% of that of the Rayleigh scattering, the difference between the correction for fluorescence and that for anisotropy according to equation (2) lies virtually within the limits of experimental error. Quite obviously, in both cases the correction factors C are in no way related with the parameter of optical anisotropy δ.

Utiyama[1] applies the correction for optical anisotropy also to the reported data on light scattering from aqueous solutions of polyampholytes[6] and gelatin[7]. He chooses such δ (or C) values which straighten the concave angular dependences of scattered light also in these cases. We are not quite sure, however, that the concave shape of angular dependences is due in these systems to the optical anisotropy of the polymer or that it is connected at all with the depolarization of scattered light; the $R_{90}(H,h)$ values are not given in the papers just quoted. As may be inferred from some of our data[8], the cause of concave radiation dependences, e.g., in aqueous polyelectrolyte solutions may be sought in the intermolecular destructive interference of scattered light in partly structured solutions, without any depolarization being operative.

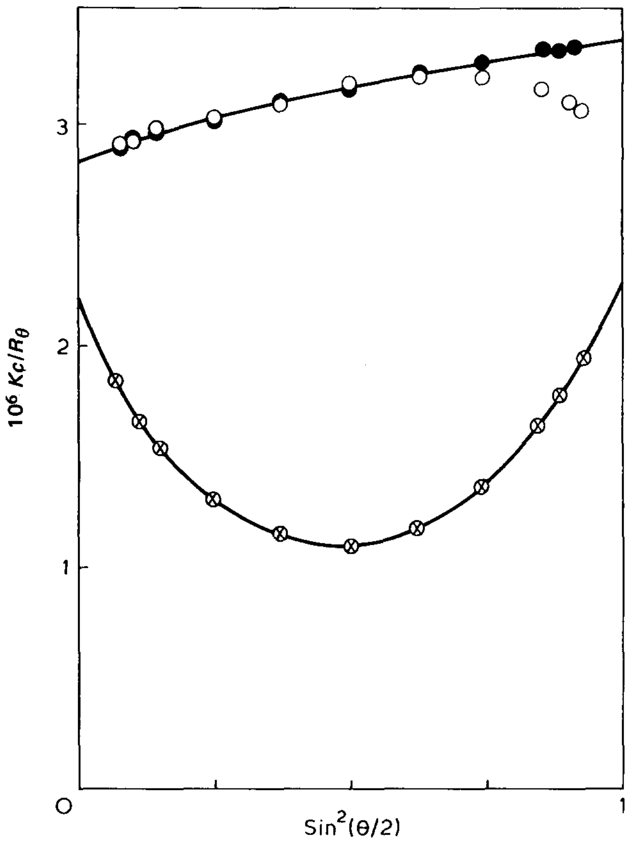

Figure 1 Apparent optical anisotropy of isotactic poly(methyl methacrylate) in n-butyl acetate. Radiation envelopes of scattered light in the case where the primary beam passes through the meniscus of solution (⊗) and through solution only (●), and radiation envelopes formally corrected (○). Polymer concentration 4.27×10^{-3} g/ml, $M_w=420\,000$; $\lambda_0=546$ nm, $t=25°$C, $dn/dc=0.097$ ml/g

Corrections of the type of equations (1–3) appear to rearrange all concave angular dependences of light scattering from polymer solutions to the usual shape irrespective of the cause of the phenomenon. However, the correction assumes physical meaning only if there demonstrably exists an optical anisotropy of the dissolved macromolecules (or, after adjustment, also for fluorescence). In other cases, it is not justified. The described reflection of the primary beam from the surface of solution is an example of an experimental artefact which in practice may be mistaken for the genuine optical anisotropy of macromolecules.

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