Nucleophilic substitution onto poly(methylmethacrylate):
4. Dilute solution properties of substituted polymethacrylates

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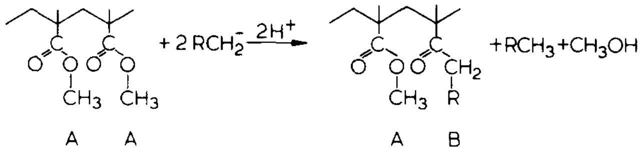
The morphological and hydrodynamic properties of a series of homogeneous fractions of substituted poly(methylmethacrylate) (A units) bearing keto-β-functional groups (B units) of the general structure $-COCH_2R$, with $R = SO_xCH_3$ ($x = 1,2$) or $SO_2N(CH_3)_2$, were investigated by intrinsic viscosity, light scattering and partial specific volume measurements in dimethylformamide (DMF) solution at 25°C. For molar substitution degrees $\overline{DS}_m < 0.5$, the copolymers behave as flexible random coils. The Stockmayer–Fixman–Yamakawa analysis of the $[\eta]$–$\bar{M}_w$ data leads to slightly higher unperturbed dimensions K_0 and steric factor σ than those for PMMA, and to stronger chain expansion as a result of the weak hydrogen bonding between DMF and $COCH_2R$ units and a positive χ_{AB} interaction parameter. For $\overline{DS}_m > 0.5$ however, copolymers bearing $COCH_2SO_2N(CH_3)_2$ groups behave as worm-like chains, as derived from the Fujii–Yamakawa analysis of the $[\eta]$–$\bar{M}_w$–$\bar{v}$ data: the persistence length increases from 380 to 570 Å within the $\overline{DS}_m$ range 0.57–0.75. This transition from a random coil to a worm-like chain for $\overline{DS}_m > 0.5$ was tentatively correlated with the accumulation of B units in sterically hindered and self-associated short blocks of average length $l_B \geqslant 1.6$ which provide drastically increased rigidity to the copolymer chain.

Keywords Substituted polymethacrylates; keto-β-sulphur groups; dilute solution properties; conformational transition

INTRODUCTION

In previous communications[1–3] we presented a survey of nucleophilic substitution of primary organolithium reagents RCH_2Li onto poly(methylmethacrylate) (PMMA) as a general route for the synthesis of random ketonic AB copolymers (A, MMA; B, keto-β-functional unit), according to the following general scheme:



with $R = SC_6H_5$, SO_xCH_3 ($x = 1,2$) and $SO_2N(CH_3)_2$.

In well selected experimental conditions this process may be remarkably free from side reactions[2]. It thus allows an easy preparation of copolymers of a similar number-average degree of polymerization ($\overline{DP}_n$) and of the same tacticity as the PMMA precursor, the molar substitution degree ($\overline{DS}_m$) being merely monitored by the initial ratio $[RCH_2Li]_0/[\text{ester function}]_0$ for $\overline{DS}_m < 0.66$. Moreover, a sufficiently high $\overline{DP}_n$ for the PMMA precursor and autoretarded kinetics for the reaction process[4,5] together contribute to the narrowing of the fluctuations in composition of the copolymers which show a very good chemical homogeneity[3]. Here we have focussed our interest on the study of the morphological and hydrodynamic properties of a series of homogeneous copolymer fractions in dimethylformamide (DMF), selected as a fairly good solvent for all the samples under study. Special emphasis was placed on two complementary points: (a) for a given B unit, $R = SO_2N(CH_3)_2$, the analysis of the influence of copolymer composition ($O < \overline{DS}_m < 0.80$) and microstructure (distribution of B units) and (b) for a given composition, $\overline{DS}_m = 0.27 \pm 0.03$, the analysis of the influence of the chemical structure of the B unit, $R = SO_x(CH_3)$ with $x = 1,2$ and $SO_2N(CH_3)_2$. A molecular interpretation of chain solvation and rigidity will be tentatively proposed, on the basis of a ^{1}H-n.m.r. study of the specific hydrogen-bonding interactions between DMF and low molecular weight model compounds $(CH_3)_3CCOCH_2R$[4,6], and on the basis of the copolymer microstructure, respectively.

EXPERIMENTAL

Characterization of the copolymer fractions

The copolymer fractions are predominantly cosyndiotactic[2] ($I = 0.05$, $H = 0.37$, $S = 0.58$), and cover a molecular weight range from 0.3 to 3.5×10^5 with polydispersity indexes $\bar{M}_w/\bar{M}_n$ of about 1.2–1.3, as supported by gel permeation chromatography. All their

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molecular characteristics $\overline{DS}_m$, $\bar{M}_w$ and $[\eta]$ in DMF solution at 25°C are reported in previous communications[1,3], but for samples R-5 and R-10 ($R=SO_2N(CH_3)_2$, $\overline{DS}_m=0.573$ and 0.755 respectively) (see Appendix). The partial specific volumes of the copolymers were measured in DMF solution at 25°C on a digital densimeter ANTON PAAR KG model DMA-02.

Specific properties of the model compounds $(CH_3)_3CCOCH_2R$ in DMF solution

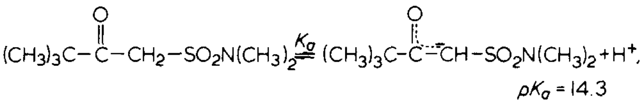
The DMF-model compound systems were studied by potentiometry for quantitative determination of the carbon acidity of the solutes (pK_a), and by ^{1}H-n.m.r. spectroscopy for a semi-quantitative analysis of the specific solute–solvent interactions through hydrogen bonding. Experimental methods are detailed elsewhere[4].

RESULTS AND CALCULATION METHODS

Mark–Houwink–Sakurada (MHS) relationships $[\eta]=K\bar{M}_w^v$

The light scattering and intrinsic viscosity measurements carried out in DMF solution at 25°C do not require any specific comment except highly substituted PMMA $\overline{DS}_m>0.5$, $R=SO_2N(CH_3)_2$. In this case for the more dilute solution ($c<0.5\%$) the Huggins plots $\eta_{sp}/c=[\eta]+k'[\eta]^2c$ do show an upward curvature similar to that observed for polyelectrolytes[7], as illustrated in *Figure 1* for sample R-5.

Ionization of the copolymer B units is probably restricted to a very low extent, as suggested by the high value of the acidity constant obtained in DMF solution for the low molecular weight model compound:



$$(CH_3)_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-SO_2N(CH_3)_2 \overset{K_a}{\rightleftharpoons} (CH_3)_3C-\overset{\overset{\displaystyle O}{\vdots}}{C}\text{---}\bar{C}H-SO_2N(CH_3)_2+H^+,\quad pK_a=14.3$$

This may be sufficient to induce weak polyelectrolyte effects, but it is not possible to exclude completely some other, and still non identified, contributions to the observed viscometric behaviour. Atactic poly(2-vinylpyridine) does show the same trends in DMF solution for instance[8], and here again ionization of the polymeric chain which is generally put forward may appear to be highly questionable. Extrapolation of the experimental viscometric data obtained at higher concentration according to the Huggins plot, or analysis of the data according to the Yuan–Dougherty–Stivala relation[9] (YDS) $\eta_{sp}/c=[\eta]_\infty\ (1+kc^{-0.5})$, allows determination of the intrinsic viscosity $[\eta]$ without any ambiguity: the identity $[\eta]_{c\to 0}(\text{Huggins})=[\eta]_{c\to\infty}(\text{YDS})$ is well obeyed, as is clearly shown in *Figure 1*.

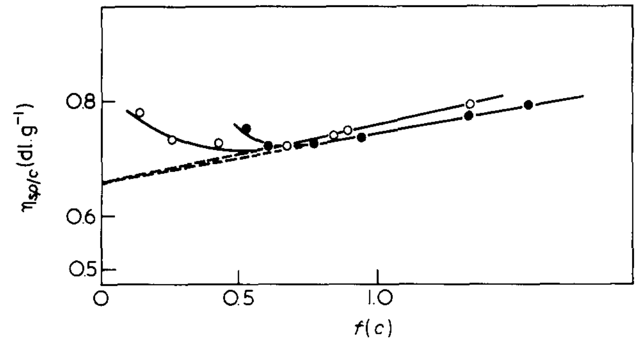


Figure 1 Variations of reduced viscosities (DMF, 25°C) with concentration for the copolymer R–5 fraction of $\bar{M}_W=1.01\times10^5$: (●), $f(c)=c$, Huggins plot; (○), $f(c)=0.5\times c^{-0.5}$, Yuan–Dougherty–Stivala plot[9]

The values of the parameters K and v of the MHS relationship and of the partial specific volumes $\bar{v}$ (DMF, 25°C) are collected in *Table 1*.

For a given $\overline{DS}_m$ of ~0.27, the intrinsic viscosities of the copolymers are nearly independent of the chemical structure of the ketonic B unit. Short and long range interactions are not sensitive to the nature of the terminal R groups all of which belong to a homologous series of sulphur functions.

For a given B structure, $R=SO_2N(CH_3)_2$, progressive substitution onto the PMMA precursor leads to an increase in intrinsic viscosities and a decrease in the partial specific volumes $\bar{v}$ (see *Figures 2* and *3*).

Chain expansion probably results from both short and long range interactions: better solvation of the copolymer through DMF-B hydrogen bonding interactions, and rigidification of the structure arising from A-B heterocontacts and from enhanced steric hindrance provided by the bulky B lateral groups (see Discussion). The characteristic sigmoidal shapes of the variations of the exponent v with $\overline{DS}_m$ and of the corresponding variations of the intrinsic viscosities plotted for copolymers of constant $\overline{DP}_n$ (see *Figure 3*) are of special interest. The introduction of only a small fraction of B units in the PMMA chain is sufficient to yield a strong decrease in the partial specific volume, and to transform DMF from a relatively poor solvent for PMMA ($v=0.65$) to a very good solvent for the copolymers ($v=0.77$) for $\overline{DS}_m=0.145$). Moreover, the enhanced increase of $[\eta]$ for $\overline{DS}_m$ values of ~0.45 together with the high values of the exponent v, $v>0.9$ for $\overline{DS}_m>0.5$, suggest a

Table 1 MHS relationships $[\eta]=K\bar{M}_W^{\nu}$ and partial specific volumes $\bar{v}$ of substituted PMMA in DMF solution at 25°C

Sample	R	$\overline{DS}_m$	$\bar{M}_W\times10^{-5}$	$r(n)^a$	ν	$K\times10^5$	$\bar{v}$ ml. g^{-1}
PMMA[b]	–	0	0.8–3.1	0.999 (5)	0.65	17.30	0.8328
R–12	$SO_2N(CH_3)_2$	0.142	0.4–2.4	0.997 (9)	0.77	4.80	0.7778
R–16	$SO_2N(CH_3)_2$	0.240	0.3–2.6	0.999 (9)	0.77	5.16	0.7641
R–3	$SO_2N(CH_3)_2$	0.395	0.3–2.2	0.998 (11)	0.78	5.46	0.7481
R–5	$SO_2N(CH_3)_2$	0.573	0.4–1.7	0.999 (8)	0.93	1.47	0.7334
R–10	$SO_2N(CH_3)_2$	0.755	0.5–1.3	0.998 (6)	0.99	0.69	
R–22	SO_2CH_3	0.299	0.3–3.5	0.997 (11)	0.79	5.15	
A–3[c]	$SOCH_3$	0.283	0.7–2.5	0.995 (6)	0.78	4.83	

[a] $r(n)$ correlation coefficient of the least square linear regression analysis of the experimental data obtained in n solvents
[b] and [c] calculated from literature data given in ref. 10 and from our previous work ref. 1, respectively

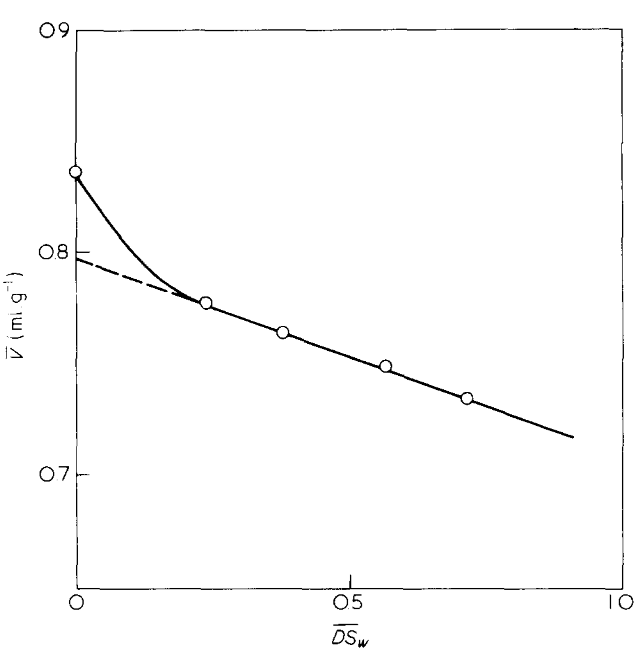


Figure 2 Variations of partial specific volume $\bar{V}$ ml.g^{-1} (DMF, 25°C) of copolymers R = $SO_2N(CH_3)_2$ with composition ($\overline{DS}_w$, weight fraction of B unit in the copolymer chain)

conformational transition from a flexible random coil ($\nu \leqslant 0.8$[11]) to a worm-like chain[12], rigid rods leading to still higher ν values ($\nu = 1.4$–1.6 [13]).

Derivation of the morphological and hydrodynamic parameters of the copolymers from the MHS relationships

Flexible random coils. ($\overline{DS}_m < 0.5$) Among the many semi-empirical derivations of the values for the unperturbed dimensions and for the polymer–solvent interaction parameters from the MHS relations obtained in good solvents[14], we have selected two complementary methods:

(1) Stockmayer–Fixman equation[15] in its modified form by Yamakawa *et al.*[16] (SFY relationship)

$$[\eta]\bar{M}_w^{-0.5} = 1.05\, K_\theta + 0.287\varphi_0 B\, \bar{M}_w^{0.5} \qquad (1)$$

(2) Bohdanecky–Cowie equation[14,17] (BC relationship) relationship)

$$[\eta]\bar{M}_w^{-0.5} = [\varphi(\varepsilon)/\varphi_0]K_\theta + 0.9166[\varphi(\varepsilon)/\varphi_0]K_\theta.k^{7/10}.\bar{M}_w^{7/20} \qquad (2)$$

with $\varphi(\varepsilon)/\varphi_0 = 1 - 2.63\varepsilon + 2.86\ \varepsilon^2$, $\varepsilon = (2\nu - 1)/3$ $k = 0.33$ $B\varphi_0/K_\theta$ $k = 0.33$ B φ_0/K_θ, φ_0 is the Flory constant, $\varphi_0 = 2.7 \times 10^{21}$ for polydispersity indexes $\bar{M}_w/\bar{M}_n$ of 1.25[18].

K_θ yields the unperturbed dimensions of the chain:

$$K_\theta = [\eta]_\theta \bar{M}_w^{-0.5} = \varphi_0 \left[\frac{\bar{r}_0^{\,2}}{\bar{M}_w}\right]^{1.5}$$

B is the polymer–solvent interaction parameter.

The SFY equation (1) remains valid over a wide viscosimetric expansion range ($0 < \alpha_\eta^3 < 2.5$), while the BC equation (2) takes into account the fact that the influence of the excluded volume is greater on the statistical than on the hydrodynamic radius of the chain according to Ptitzyn and Eizner[19]: $\varphi(\varepsilon) = f(\varphi_0, \nu)$. The characteristic structural parameters, such as the statistical element length b and the steric factor σ of the chain, may be easily derived from the K_θ values in the classical way[1], assuming for copolymers, an average monomer unit of molecular weight:

$$M = M_A(1 - \overline{DS}_m) + M_B\, \overline{DS}_m$$

Worm-like chains. ($\overline{DS}_m > 0.5$) We have tentatively interpreted the viscosimetric behaviour of the highly substituted copolymers in a semi-quantitative way, assuming that their conformation is similar to that of a worm-like chain, as recently analysed by Yamakawa and Fujii[20,21]. The semi-rigid chain of molecular weight M and of degree of polymerization N is described as a continuous cylinder of contour length L (M_L molecular weight by unit length $= M/L$, a statistical element identical to the projection of the repetitive segment on the contour length, $L = Na$) and of diameter d characterized by the Kuhn statistical segment length q (persistence length $l = 2q$). Combining expressions that Bohdanecky *et al.*[22] and Fujita *et al.*[23] derived independently from previous theory, and assuming as Fujita *et al.*[24] that the specific hydrodynamic volume of the worm-like chain is not too different from its partial specific volume in solution $\bar{v}$, one obtains the following relations:

$$\bar{M}_w^{0.5}[\eta]^{-1} = A_\eta \bar{M}_w^{-0.5} + B_\eta \qquad (3)$$

with

$$B_\eta = \varphi'^{-1}_\infty(M_L, l^{-1})^{1.5}\ , \quad \varphi'_\infty \simeq \varphi_\infty = 2.6 \times 10^{21} \qquad (4)$$

$$A_\eta = B_\eta(M_L.l)^{0.5}.\,A_0 \qquad (5)$$

$$\bar{v} = \pi N_A d^2/4M_L \qquad (6)$$

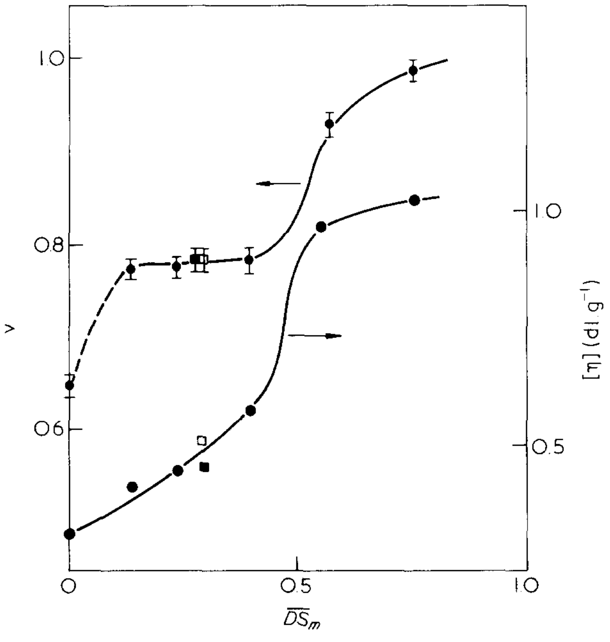


Figure 3 Variations of MHS exponents ν and of intrinsic viscosities $[\eta]$ of copolymers of $\overline{DP}_n = 10^3$ with composition: (●), R = $SO_2N(CH_3)_2$; (□), R = SO_2–CH_3; (■), R = $SOCH_3$

Equation (3) allows direct determination of the coefficients A_η and B_η, together with the ratio $M_L.l^{-1}$ from viscosimetric and molecular weight data along. Moreover, according to Bohdanecky *et al.*[22], for most of the semi-rigid polymers the A_0 coefficient is of the form:

$$A_0 = -1.23 - 1.97\,\mathrm{Ln}\,(d.l^{-1}) \qquad (7)$$

Combination of equations (4), (6) and (7), and combination of equations (4) and (5) lead to two expressions which are functions of one single variable l, and this allows its determination by successive iterations:

$$A_0 = -1.23 - 0.985\,\mathrm{Ln}[(M_L.l^{-1}) \times 4\bar{v}(\Pi N_A)^{-1} \times l^{-1}]$$
$$= A_\eta \varphi (M_L.l^{-1})^{-2} l^{-1}$$

The values of the parameters d and l thus evaluated are strongly dependent on the necessary simplifying assumptions previously made, and they are to be considered critically and cautiously. Their order of magnitude is however well ascertained.

DISCUSSION

Unperturbed dimensions and rigidity of the moderately substituted PMMA

For $\overline{DS}_m \leqslant 0.4$, the copolymers behave as well solvated flexible random coils in dilute DMF solution. SFY and BC linearization methods are illustrated in *Figures 4* and *5*, and the values of the characteristic structural parameters K_θ, b and σ are collected in *Table 2.* The differences introduced by the SFY and BC relations are not negligible, especially for K_θ, but this is not surprising when taking into account the semi-empirical character of the equations and the approximations involved[14]. However, some significant trends may be pointed out, mainly for the statistical element b and the steric factor σ.

For a given $\overline{DS}_m$ of $\sim 0.27 \pm 0.03$, the copolymer steric factor σ is nearly independent of the nature of the terminal R group which is probably too remote from the main chain to contribute to the restriction of free rotation of the backbone segments. Moreover, the fluctuations of the interaction parameter χ_{AB} between unlike monomer units are probably fairly small within this homologous series of keto-β-functionalized structures.

For copolymers bearing a given B unit, $R = SO_2N(CH_3)_2$, σ is a slightly increasing function of the $\overline{DS}_m$: it increases by $\sim 20\%$ when $\overline{DS}_m$ changes from 0.14 to 0.39 (see *Figure 6*).

This feature may reflect enhanced steric hindrance along the chain as a result of progressive substitution of the ester functions by bulkier lateral groups, and rigidification of the structure owing to A–B repulsive short-range interactions (see later). Comparison between copolymers and PMMA precursor is however somewhat puzzling. The PMMA σ value, derived in the same way

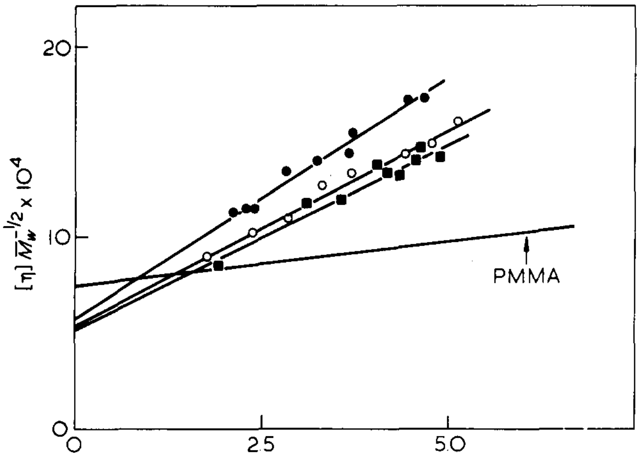


Figure 4 Stockmayer–Fixman plots of $[\eta]-\overline{M}_w$ data for copolymers $R = SO_2N(CH_3)_2$ of $\overline{DS}_m \leq 0.5$: (——) literature data for PMMA; (■), $\overline{DS}_m = 0.142$; (○), $\overline{DS}_m = 0.240$; (●), $\overline{DS}_m = 0.395$

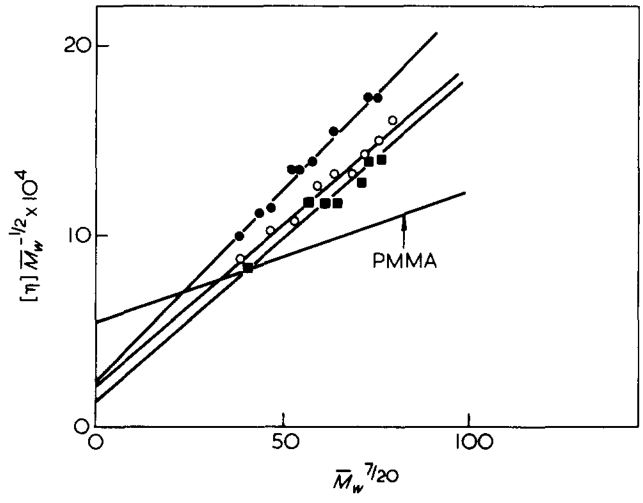


Figure 5 Bohdanecky–Cowie plots of $[\eta]-\overline{M}_w$ data for copolymers $R = SO_2N(CH_3)_2$ of $\overline{DS}_m < 0.5$. Symbols as in *Figure 4*

Table 2 Structural parameters of the various copolymers

			$K_\theta\,10^4$ dl g^{-1}		b (Å)		σ							
Sample	R	$\overline{DS}_m$	SFY	BC	SFY	BC	SFY	BC	l (Å)	l^* (Å)	d (Å)	d^* (Å)	a (Å)	a^* (Å)
PMMA	–	0	7.10	8.0	6.4	6.6	2.08	2.13						
R–12	$SO_2N(CH_3)_2$	0.140	5.07	4.45	5.9	5.0	1.92	1.61						
R–16	$SO_2N(CH_3)_2$	0.240	5.05	4.06	6.4	5.9	2.09	1.91						
R–3	$SO_2N(CH_3)_2$	0.395	5.61	4.32	7.0	6.4	2.28	2.06						
R–5	$SO_2N(CH_3)_2$	0.573							380	380	15.5	13.0	0.98	1.2
R–10	$SO_2N(CH_3)_2$	0.755							630	570	17.5	14.0	0.85	1.2
R–22	SO_2CH_3	0.290	5.65	3.68	6.6	5.6	2.12	1.81						
A–3	$SOCH_3$	0.283	5.53	4.28	6.4	5.8	2.07	1.87						

l^*, d^* and a^* are optimized values calculated to allow the best agreement between calculated and experimental MHS relationships

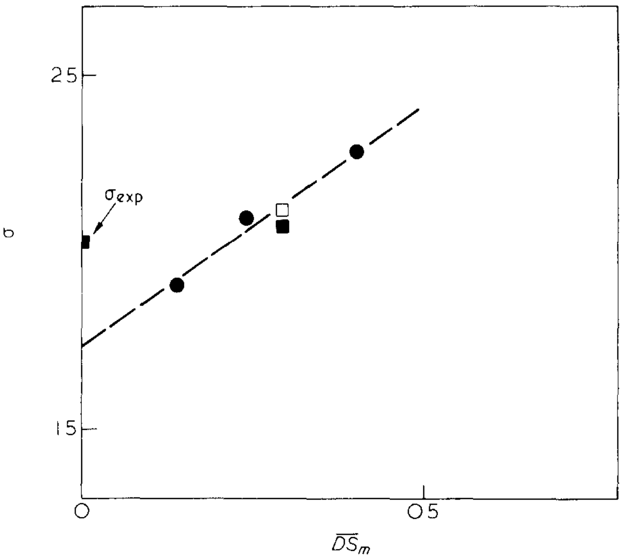


Figure 6 Variations of steric factor σ of copolymers of $\overline{DS}_m < 0.5$ with composition. Symbols as in *Figure 3*

from SFY or BC equations applied to viscosimetric data in DMF solution at 25°C[10], is ~2.10, which is significantly higher than that obtained by extrapolation of the copolymers σ values to $\overline{DS}_m \rightarrow 0$, $\sigma = 1.75$ (see *Figure 6*). Non-monotonous variations of the chain rigidity involving some conformational transition within the $\overline{DS}_m$ range 0–0.2 seem highly questionable. However, the extrapolated σ value is quite close to the average value calculated according to the SF method for PMMA in a series of non polar or weakly polar solvents, $\bar{\sigma} = 1.70$[25]; this good agreement however may be merely incidental. As already outlined by Dondos and Benoit[25], all the semi-empirical analysis of the MHS relationships are rigorous for non polar systems only, and they do not apply strictly to our copolymer–DMF solutions characterized by weak but significant hydrogen-bonding interactions (see later) and by the strongly self-associated structure of the solvent[26]. Comparison restricted to the various polar copolymers may still remain meaningful, but the choice of the non polar PMMA as a reference polymer is probably very hazardous.

Structural parameters of the highly substituted PMMA. ($\overline{DS}_m > 0.5$, $R = SO_2N(CH_3)_2$) The dilute solution properties of highly substituted PMMA bearing keto-β-sulphonamide groups (R-5 and R-10 samples of $\overline{DS}_m = 0.573$ and 0.755 respectively) were tentatively interpreted according to the theory of semi-rigid worm-like chains[20,21]. Linearization of the experimental [η] and $\bar{M}_w$ data according to equation (3) is illustrated in *Figure 7*.

As an independent check of the self-consistency of the results, the directly derived values of the *l*, *a* and *d* structural parameters were used to re-calculate the intrinsic viscosities of the copolymers, using the general equation: $[\eta] = \varphi L^{3/2} \bar{M}_w^{-1}$ and adjusting the φ coefficient, which is a function of *L* and *d*, with suitable values from the numerical compilation of Yamakawa and Fujii[21]. These primary *l*, *a* and *d* values were further optimized to allow a better agreement between the experimental and the calculated MHS relationships: see *Table 2* and *Figure 8*.

A thorough and quantitative analysis of these optimized values is not possible on the basis of our limited experimental results, but they may be critically discussed as follows. The length of the statistical elements $a^* = 1.2$ Å is of the order of magnitude of the length of the covalent C–C single bond, and seems reasonable for a methacrylic main chain. The diameter of the cylinder including the worm-like chain, $d^* = 13$–14 Å, which is in fairly good agreement with the maximum dimension of about 10 Å for the unsolvated keto-β-sulphonamide B unit estimated on Corey–Pauling–Koltun molecular models. The increase of the persistence length l^* from 380 to 570 Å when $\overline{DS}_m$ changes from 0.573 to 0.755 is consistent with the simultaneous increase of steric hindrance along the chain. Finally, the mean square radius of gyration calculated from $L^* = Na^*$ and q^* optimized values according to Benoit and Doty[27] are not greater than 250 Å for the highest molecular weight copolymers: this feature is in good agreement with the negligible dissymmetry observed in the light scattering experiments.

The origin of the conformational transition from a flexible random coil to a worm-like chain may be tentatively correlated with copolymer microstructure we analysed directly by ^{1}H-n.m.r. spectroscopy at 250 MHz, or derived from the u.v. study of intramolecular cyclization of BB diads in basic protic medium, as detailed elsewhere[4,5]. Distribution of B units is illustrated in *Figure 9* in terms of the various B centred triads, and we have compared the simultaneous increase of intrinsic viscosity $[\eta](\overline{DP}_n = 10^3)$ and the mean chain length $\bar{l}_B$ of B blocks in *Figure 10*.

It is clear that for $\overline{DS}_m$ values greater than ~0.5, the fraction of isolated B units $F(A\dot{B}A)$ decreases to values lower than 0.35 and that $\bar{l}_B$ increases rapidly to values higher than 1.6. For sample R-5 with $\overline{DS}_m = 0.573$, which is the first to show a worm-like chain behaviour, $F(A\dot{B}A)$ is as low as 0.22 and $\bar{l}_B$ is ~2. The enhanced rigidity of the copolymers for $\overline{DS}_m > 0.5$ may be thus correlated with the accumulation of B units in diads or longer blocks increasing the mean chain length $\bar{l}_B$ to values close to or higher than 2. However, an increase in the molar volume of the lateral group inducing a corresponding σ increase in vinyl and acrylic polymers is well known[25], but a brief

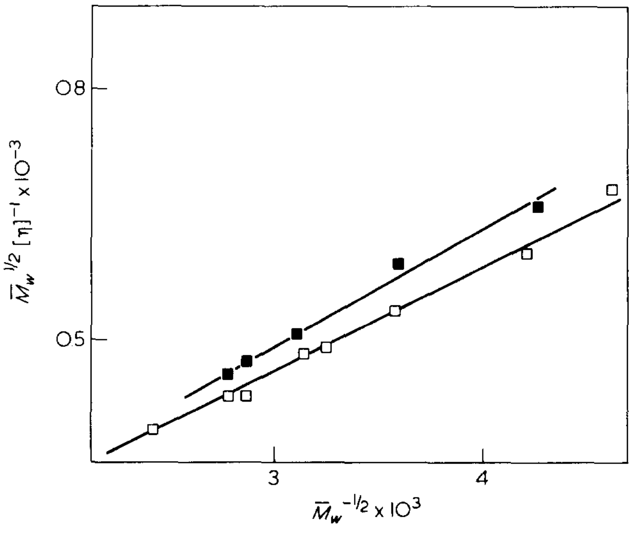


Figure 7 Yamakawa–Fujii plots of $[\eta]$–$\bar{M}_w$ data for copolymers $R = SO_2N(CH_3)_2$ of $\overline{DS}_m > 0.5$: (□), $\overline{DS}_m = 0.573$; (■), $\overline{DS}_m = 0.755$

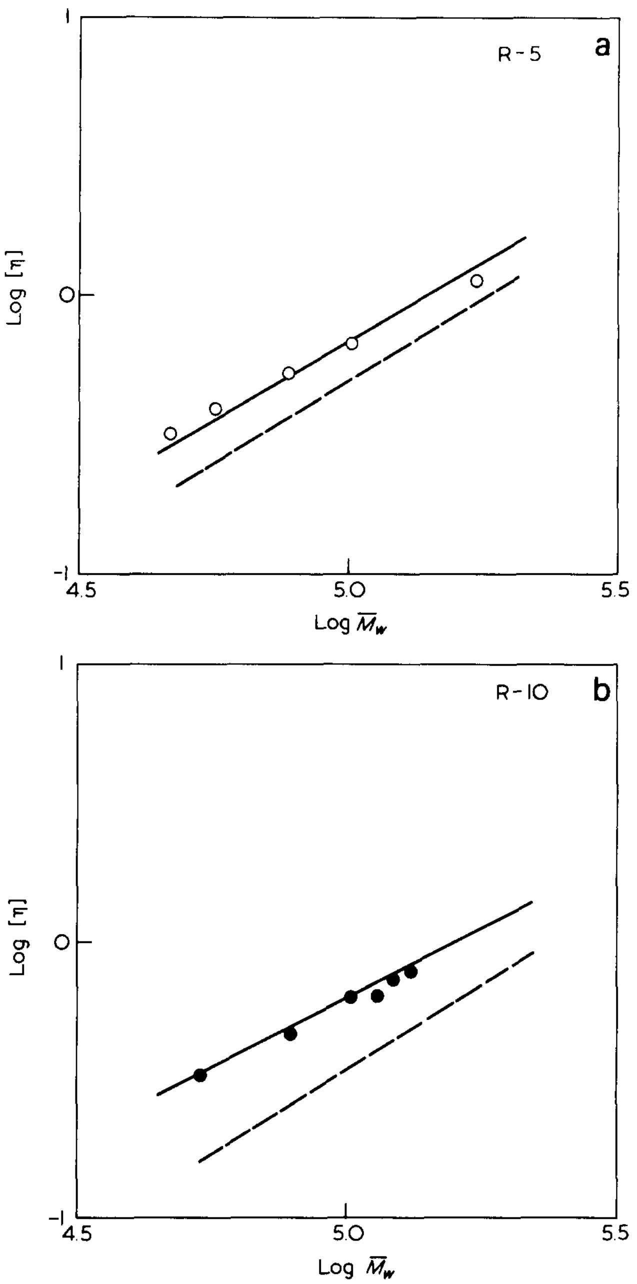


Figure 8 MHS relationships for semi-rigid copolymers (a) R–5 and (b) R–10: (●), experimental points. Linear variations derived from the primary *l*, *d* and *a* (· · · ·) and from the optimized *l**, *d** and *a** values (——)

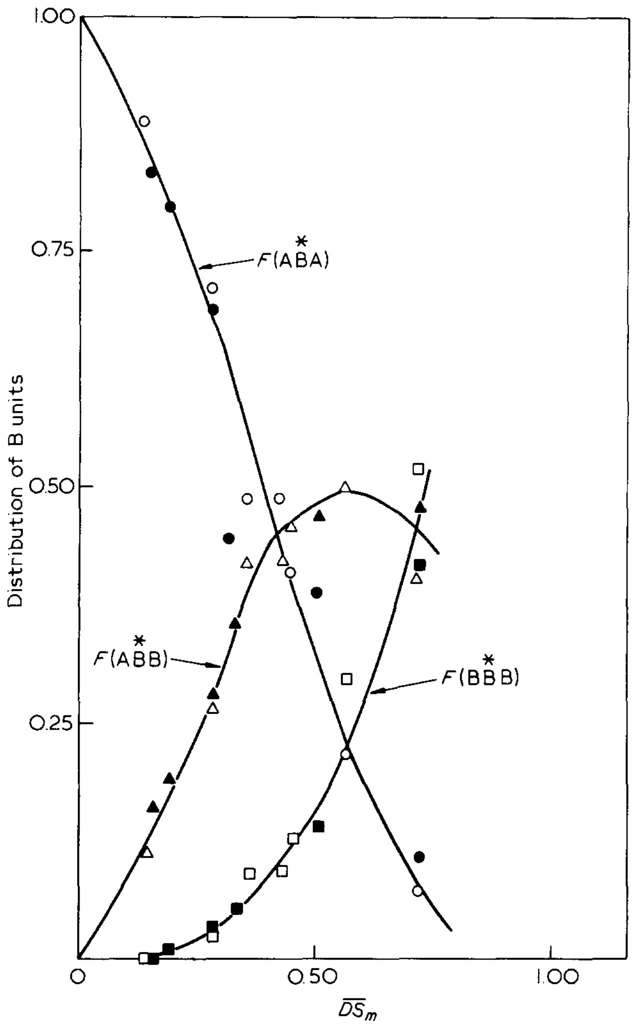


Figure 9 Distribution of B units in the copolymer chains. (●, ○): $F(A\overset{*}{B}A)$; (▲, △): $F(A\overset{*}{B}B)$; (■, □): $F(B\overset{*}{B}B)$. Filled and open symbols for R = $SO_2N(CH_3)_2$ and SO_2CH_3 respectively

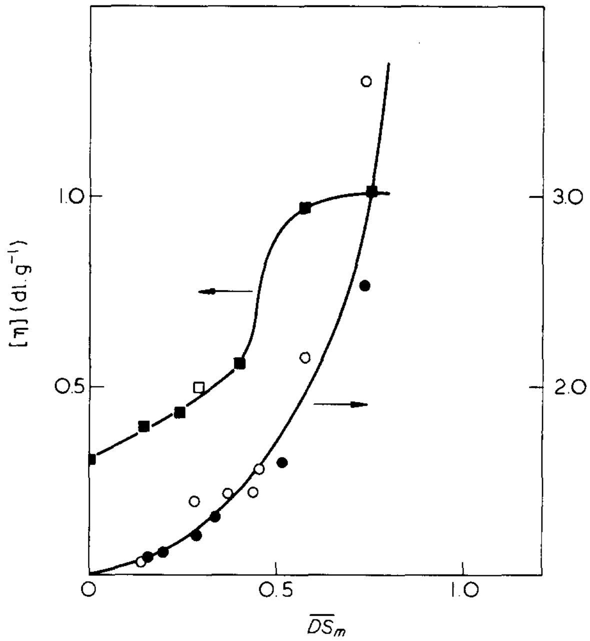


Figure 10 Variations of intrinsic viscosity [η] of copolymers of $\overline{DP}_n = 10^3$ (■, □) and of the mean chain length $\bar{l}_B$ of B blocks (●, ○) with composition. Filled and open symbols for R = $SO_2N(CH_3)_2$ and SO_2CH_3

survey of the literature[18] shows that, even for these high σ polymers, the conformation of a random coil in solution is the general rule, as for poly(*t*-butylmethacrylate), $\sigma = 3.45$ [28], or for poly(tritylmethacrylate), $\sigma = 2.97$ [29]. Thus steric hindrance provided by the bulky B units is probably not the major factor in copolymer rigidity. From a ^{1}H-n.m.r. study detailed elsewhere[4,5] we have shown that 1,3-bis(dimethylaminosulphonylacetyl) propand $(CH_3)_2N$-$SO_2CH_2CO(CH_2)_3$-$COCH_2SO_2\ N(CH_3)_2$, selected as a dimeric model of BB diads in copolymers, shows intramolecular self-association between the keto-β-sulphonyl groups. This feature suggests that the worm-like chain behaviour of copolymers of $\overline{DS}_m > 0.5$ may arise mainly from the self-associated structure and the intrinsic rigidity of BB diads or longer blocks within the chain. This situation may be similar to that of poly(*p*-

Table 3 Copolymer–solvent interactions in DMF at 25°C

Sample	R	$\overline{DS}_m$	α_η^3 [a]	$B \times 10^{28}$ [b]	χ
PMMA[c]	–	0	1.30	6.1	0.480
R–12	$SO_2N(CH_3)_2$	0.140	2.20	26.8	0.397
R–16	$SO_2N(CH_3)_2$	0.240	2.40	26.5	0.394
R–3	$SO_2N(CH_3)_2$	0.395	2.60	32.3	0.365
R–22	SO_2CH_3	0.290	2.45	32.5	–
A–3[d]	$SOCH_3$	0.283	2.30	29.2	–

[a] Calculated for a constant $\overline{DP}_n$ of 10^3
[b] Derived from the Stockmayer–Fixman–Yamakawa equation (1)
[c] and [d] calculated from literature data given in ref. 10 and from our previous work ref. 1, respectively

diethylphosphono-methylstyrene-co-styrene) previously described by Russian authors[30] as semi-rigid chains for $\overline{DS}_m$ as low as 0.25 ($v = 1.18$ and 0.9 in tetrachloroethane and benzene respectively).

Long range polymer-solvent interactions and intramolecular A–B short range interactions

Copolymer–solvent interactions are quantitatively measured by the B parameter (see equations (1) and (2)) which is related to the Flory interaction parameter according to[15]:

$$0.5 - \chi = 0.5\, N_A\, V_1\, B/\bar{v}^2$$

where V_1 is the molar volume of the solvent and N_A the Avogadro's number. Moreover Stockmayer *et al.*[31] have expressed the copolymer solvent χ interaction parameter in the form of additive terms according to:

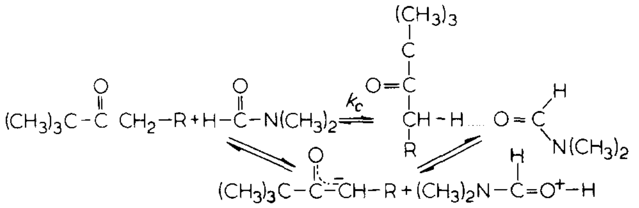
$$\chi = \chi_A(1 - \overline{DS}_m) + \chi_B\overline{DS}_m - \chi_{AB}\overline{DS}_m(1 - \overline{DS}_m)$$

where χ_A, χ_B and χ_{AB} are the A–DMF, B–DMF and A–B interaction parameters respectively. The knowledge of χ_A from literature data related to pure PMMA[10] allows calculation of the interaction parameters χ_B and χ_{AB} provided the experimental B values are accessible for at least two copolymers of different composition. The estimated values are however only approximate, and the χ_{AB} parameter may show a strong dependence on the solvent nature. The B and χ values and the viscosimetric expansion coefficient $\alpha_\eta^3 = [\eta]/[\eta]_\theta$ were calculated for a constant $\overline{DP}_n = 10^3$ and are collected in *Table 3*.

For a given R group, $R = SO_2N(CH_3)_3$, the variations of B, χ and α_η reflect enhanced expansion and solvation of the chain with progressive substitution of the PMMA precursor. DMF is a thermodynamically poor solvent for PMMA, $\chi_A = 0.48$, and increased expansion of the copolymer chain results from both better solvation of B units, $\chi_A = 0.37 \pm 0.08$, and from repulsive A–B short-range interactions between the dissimilar monomer units as revealed by the rather high positive χ_{AB} value of $\sim 0.12 \pm 0.05$.

For a given $\overline{DS}_m$ of 0.27 ± 0.03, the B and χ values are fairly similar whatever the chemical nature of the B unit is, suggesting that χ_B and χ_{AB} interaction parameters do not show very significant differences for keto-β-sulphoxide, sulphone and sulphonamide structures.

A molecular interpretation of copolymer solvation, and especially of the χ_B term, may be tentatively derived from an ^{1}H-n.m.r. study of the model $(CH_3)_3CCOCH_2R$–DMF system, as detailed elsewhere[4,6]. The chemical shifts of the acidic methylenic group $\delta(COCH_2R)$ are a decreasing function of the solute concentration, characteristic of solute–solvent hydrogen bonding interactions (k_c), which are not to be considered as a necessary preliminary step in the carbon acid ionization (K_A):



Assuming a 1 to 1 complex, the semi-quantitative analysis of the dilution curves $\delta(COCH_2R) = f(c)$ within the solute molar fraction range 0.01–0.6 yields an estimate of the complexation equilibrium constant k_c, together with the frequency shift $\Delta\nu_c$ (Hz) between the hydrogen-bonded complex and the free forms of the various solutes; $\Delta\nu_c$ may be considered as representative of the hydrogen bond strength[4,6].

The k_c and $\Delta\nu_c$ values collected in *Table 4* are relatively small, and they show that hydrogen bond interactions between DMF and these C–H donors remain weak and cannot be compared with those of the more powerful O–H or N–H donors[32]. Nevertheless, for the homologous series of keto-β-functionalized models there is a good correlation between the hydrogen bonding complexation and the ionization; and moreover, the higher the acidity, the higher the hydrogen bond strength. Keto-β-sulphone and sulphonamide groups are nearly equivalent, while the keto-β-sulphoxide is a weaker carbon acid and hydrogen bond donor: this is in good agreement with the well known inductive effect scale, sulphoxide < sulphonamide ⩽ sulphone. These small differences may be levelled off in copolymers, since similar polymeric backbone and similar MMA neighbouring group effects contribute to the definition of the polarity of the microenvironment of the B sites on the chain[5].

CONCLUSION

The study of the dilute solution properties in DMF of a series of homologous substituted PMMA bearing keto-β-sulphonamide groups has shown, as the most interesting result, a conformational transition from a flexible random coil to a semi-rigid chain occurring in a rather sharp $\overline{DS}_m$ range around 0.5. This characteristic feature is very unusual for a methacrylic random copolymer, but it is probably not a single isolated case. For instance, in the course of their studies on dilute solution properties of methylmethacrylate–acrylonitrile (AN) copolymers in polar solvents like DMF, Kalpagam *et al.*[33,34] have recently observed a very large extension of the AN rich

Table 4 Solute–solvent hydrogen bonding interactions and carbon acidities of the model compounds $(CH_3)_3CCOCH_2R$ in DMF solution

R	k_c (l mol^{-1})	$\Delta\nu_c$ (Hz)	pK_a
$SOCH_3$	<0.1	19	15.6
SO_2CH_3	0.34	66	14.1
$SO_2N(CH_3)_2$	0.22	54	13.3

copolymer chains (mole fraction 0.657), as particularly revealed by exponent v values close to 1. These unexpected features were attributed to 'unusual short range interactions'. The analysis of the experimental data however was performed according to the Stockmayer–Fixman equation, even in the case of $v=1$: the physical meaning of the thus calculated structural parameters may be highly questionable, as clearly recognized by the authors themselves. The very low K_θ and σ values ($K_\theta<1$ or negative in some cases, $\sigma<1$) and even more the strongly negative values of the excess interaction parameter χ_{AB} ($-0.6<\chi_{AB}<-0.3$) may appear quite unrealistic.

The behaviour of this MMA–AN copolymer could probably be better described within the theoretical framework developed for worm-like chains, as with highly substituted PMMA.

Finally the major interest in a precise knowledge of the copolymer microstructure and of the solute–solvent interactions, as analysed on low molecular weight model compounds, is again re-emphasized for a thorough and comprehensive study of dilute solution properties of random copolymers.

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APPENDIX

$[\eta]$(DMF, 25°C) and $\bar{M}_w$ experimental data for copolymers R-5 and R-10: $R=SO_2N(CH_3)_2$, $\overline{DS}_m=0.573$ and 0.755 respectively.

R-5	$[\eta]$dl.g^{-1}	1.05	0.845	0.825	0.660	0.630	0.525	0.395	0.316
	$\bar{M}_w\times10^{-5}$	1.68	1.30	1.24	1.01	0.95	0.775	0.565	0.465

R-10	$[\eta]$dl.g^{-1}	0.800	0.700	0.680	0.650	0.480	0.322
	$\bar{M}_w\times10^{-5}$	1.32	1.24	1.15	1.06	0.792	0.559