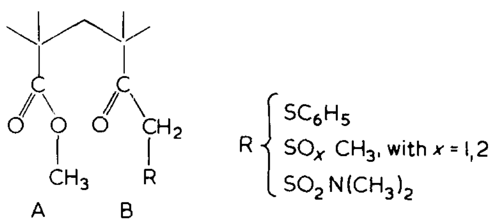
Nucleophilic substitution onto poly (methyl methacrylate): 3. Compositional homogeneity of the substituted polymethacrylates

J. J. Bourguignon, H. Bellissent and J. C. Galin
Centre de Recherche sur les Macromolécules, CNRS, 6, rue Boussingault, 67083 Strasbourg Cedex, France
(Received 28 March 1977)

The chemical homogeneity of a series of copolymers obtained by nucleophilic substitution of organolithium reagents RCH_2Li [$R = S(C_6H_5)$, $SOCH_3$, SO_2CH_3 and $SO_2N(CH_3)_2$] on a high molecular weight poly(methyl methacrylate) (PMMA, $\overline{DP}_n = 700$) has been studied by different methods, over a wide range of substitution degrees ($0.14 \leqslant \overline{DS}_m \leqslant 0.76$). 'Cross' fractionation is much more efficient than 'one direction' fractionation, and it allows the determination of $\overline{\sigma}^2$ variance values as low as 2×10^{-4} with sufficient accuracy. The light scattering method is far less sensitive in this range of low compositional polydispersity, even for a suitable system. The fairly high chemical homogeneity observed for all the copolymers, prepared either in homogeneous or heterogeneous solution, may be correlated with both the high molecular weight of the PMMA precursor and the autoretarded kinetics of the substitution process.

INTRODUCTION

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



This process is remarkably free from side reactions. It allows an easy preparation of model copolymers of the same 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 $[RCH_2Li]_0/$ [ester function]$_0$ for $\overline{DS}_m < 0.66$. On the other hand, copolymer properties are well known to depend on compositional homogeneity and on unit distribution, which are controlled, in our case, by the molecular characteristics of the polymeric precursor ($\overline{DP}_n$ and molecular weight distribution *MWD*), by the modification reaction kinetics and by the extent of substitution[4–8]. In the present work, we have focused our interest on the chemical homogeneity of the modified PMMA.

Since copolymers may present a polydispersity with respect to both molecular weight and composition, the quantitative determination of chemical homogeneity is never a routine problem, even if a number of methods are available: fractionation[9,10], density gradient sedimentation[12,13], light scattering[14], gel permeation chromatography[15,16], thin-layer chromatography[17,18] or column adsorption chromatography[19]. Each method has its own limitations, and in a number of cases the experimental results cannot be taken into account unambiguously[9,13,16,19,20]. Since the pioneering study of Rosenthal and White[21] on acetylated cellulose, 'cross' fractionation, which is probably the more reliable but the more tedious preparative method, seems to have been neglected for the analysis of chemical heterogeneity in modified polymers. On the other hand, in spite of its lower sensitivity, light scattering is probably the easiest analytical method and, in ideal cases, it is theoretically expected to give a great deal of information on copolymer structure[14]. Thus three main purposes were pursued in the present work: (a) comparison of the efficiency of 'cross' and 'one direction' fractionation; (b) analysis of the chemical homogeneity by light scattering; (c) correlation between the compositional homogeneity of the copolymers and the kinetics of their preparation process.

EXPERIMENTAL

Solvents and polymers

All the solvents were purified by distillation according to standard methods. Special care was taken for very hygroscopic solvents which were previously dried with suitable reagents. disodium benzophenone complex for tetrahydrofuran and dioxane, calcium hydride for dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP).

All the copolymers under investigation were obtained by reaction of the appropriate organolithium reagent on a radical PMMA ($\overline{M}_w = 0.95 \times 10^5, \overline{M}_n = 0.69 \times 10^5$) of predominantly syndiotactic structure (I = 0.05, H = 0.37, S = 0.58) as described previously[1-3]. The assay number in the different Tables refers to the experiment number of the preceeding communication[3].

Fractionation

The γ_1 value (volume fraction of the non-solvent in the ternary system polymer–solvent–non solvent) at the first cloud point was determined visually at room temperature, starting from 1% (wt/vol) polymer solution.

All the fractionations were carried out at 20° ± 0.1°C in a standard way by successive precipitation, adding increments of non-solvent into the polymer solution (1% wt/vol as initial concentration). Composition of every fraction was calculated from nitrogen and sulphur elemental analysis. The self-consistency of the fractionation results was checked by the comparison between the molecular parameters ($\overline{M}_w$, $[\eta]$, $\overline{DS}_m$) measured directly on the crude copolymer and the corresponding values deduced from fractionation data (% recovery, $\overline{M}_w = \sum_i w_i \times M_{w_i}$, $\overline{DS}_m = \sum_i w_i \times DS^i_m$, $[\eta] = \sum_i w_i \times [\eta]_i$): a good agreement was always observed.

The compositional distribution was characterized by two parameters: the mean square standard deviation:

$$\overline{\sigma}^2 = \Sigma_i w_i \times (DS^i_m - \overline{DS}_m)^2$$

and the symmetry of the distribution[22] $V = U^+/U^-$

where

$$U^+ = \sum_i w_i \times (DS^i_m - \overline{DS}_m)/\Sigma w_i, \text{ with } DS^i_m > \overline{DS}_m$$

$$U^- = \sum_j w_j \times (\overline{DS}_m - DS^j_m)/\Sigma w_j, \text{ with } \overline{DS}_m > DS^j_m$$

The experimental accuracy of nitrogen and sulphur elemental analysis is about 0.5%, and it implies an accuracy of about 0.7% for $\overline{DS}_m$ values; this leads to a broadening of the composition distribution, which may be estimated by an apparent $\overline{\sigma}^2$ value of about $5 \times 10^{-5} \times \overline{DS}^2_m$ for a perfectly homogeneous copolymer.

Molecular weight and intrinsic viscosity measurements

The refractive index increments were measured at room temperature on a Brice–Phoenix B.P.-1000 V differential refractometer for λ = 5460 Å. The light scattering measurements were carried out for the same wavelength at room temperature on a FICA apparatus. The accuracy of the $\overline{M}_w$ determination may be evaluated to about 5% in all cases.

The viscosity measurements on dilute DMF solutions were performed at 25°C using a FICA automatic viscosimeter. Intrinsic viscosity was calculated from extrapolation of experimental data according to the classical Huggins relationship.

RESULTS AND DISCUSSION

Comparison between 'one direction' and 'cross' fractionations of a substituted PMMA bearing keto-β-sulphonamide groups ($\overline{DS}_m = 0.366$, $\overline{M}_w = 1.43 \times 10^5$)

According to Topchiev *et al.*[23] and Teramachi *et al.*[24], the distribution of an AB copolymer of polymerization degree $\overline{\gamma}$ and substitution degree $\overline{\alpha}$ (volume fraction of B units in the AB copolymer) between the two phases of a two solvent system (solvents 1 and 2) may be described by the relation:

$$V'_{\gamma,\alpha}/V_{\gamma,\alpha} = \exp \gamma(\sigma + K\alpha)$$

$$\text{with } K = (V_1 - V'_1)(\chi_{1A} - \chi_{1B}) + (V_2 - V'_2)(\chi_{2A} - \chi_{2B})$$

where $V_{\gamma,\alpha}$ and V_i are the volume fractions of the component (γ,α) of the copolymer and of the solvent i respectively, V and V' denoting the supernatant and the precipitated phases; σ is a fractionation parameter; χ_{iA} and χ_{iB} are the i solvent interaction parameters with A and B units.

Copolymer fractionation clearly depends on both molecular weight and composition distribution, and 'one direction' fractionation (successive precipitation using a single solvent–non-solvent system) does not allow, in general, the determination of the true chemical distribution[25]. Litmanovitch *et al.*[26,27] have proposed that the actual compositional distribution may be fairly approximated by 'cross' fractionation. The copolymer is first fractionated into intermediate fractions using a given solvent–non-solvent system, and then, every intermediate fraction is further fractionated using a second system; the two fractionation systems must be characterized by K values as high as possible (sensitivity to composition) and of opposite signs.

In practice, the choice of the solvent–non-solvent systems rests upon the study of the variations of the volume fraction of the precipitant at the first cloud point (γ_1 value) in the ternary system copolymer–solvent–non-solvent (finite but low copolymer concentration) with composition for a series of homologous copolymers of different composition but of nearly the same molecular weight.

The variations of γ_1 *versus* $\overline{DS}_m$ are plotted in *Figure 1* for substituted PMMA bearing keto-β-sulphonamide groups

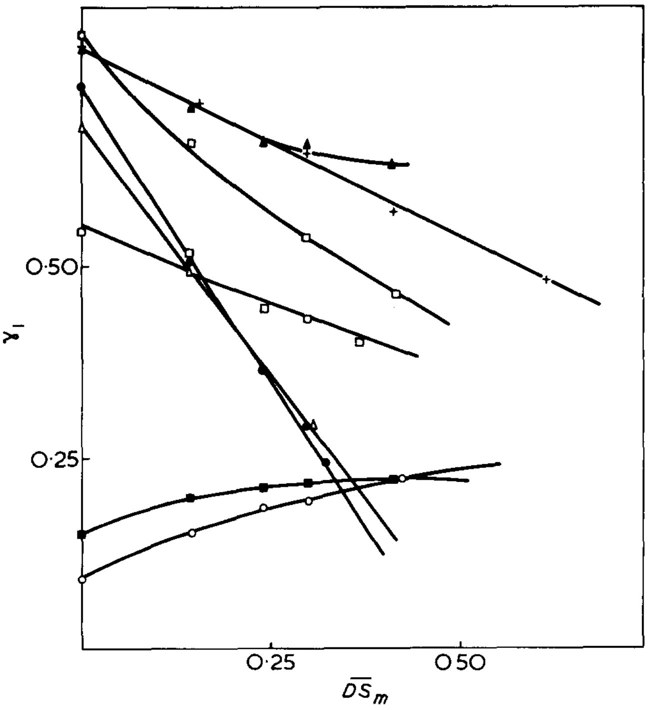


Figure 1 Variations of γ_1 values *versus* $\overline{DS}_m$ for substituted PMMA fractionated with various solvent–non-solvent systems: ●, chloroform-ethyl ether; ○, DMF–water; ■, acetone–water; □, acetone–methanol; ▲, DMF–methanol; △, chloroform–petroleum ether for R = $SO_2N(CH_3)_2$; +, DMF–methanol for R = SO_2CH_3

Table 1a Fractionation of copolymer R-19; system I, $CHCl_3$–Et_2O

Fraction no	Weight fraction, w_i × 10^2	DS_m^i
1	23.45	0.350
2	20.24	0.352
3	15.13	0.354
4	11.82	0.354
5	11.32	0.357
6	8.32	0.358
7	3.31	0.358
8	4.01	0.363
9	2.40	0.368

Copolymer recovery: 84%; $\overline{DS}_m$ crude copolymer: 0.366; $\overline{DS}_m$ from fractionation: 0.354

Table 1b Fractionation of copolymer R-19; system II, DMF-H_2O + 0.5% NH_4Cl

Fraction no	Weight fraction, w_i × 10^2	DS_m^i
1	0.83	0.368
2	5.50	0.365
3	10.72	0.357
4	5.50	0.371
5	1.38	0.361
6	10.60	0.362
7	15.30	0.358
8	18.30	0.368
9	10.45	0.368
10	13.09	0.368
11	8.26	0.390

Copolymer recovery: 90%; $\overline{DS}_m$ crude copolymer: 0.366; $\overline{DS}_m$ from fractionation: 0.366

Table 1c Fractionation of copolymer R-19; 'cross' fractionation

Fraction no.	Weight fraction, w_i × 10^2	DS_m^i	[η] (dl/g)
1-1	6.53	0.371	1.055
1-2	3.57	0.354	0.775
1-3	9.17	0.368	0.760
1-4	7.93	0.343	0.531
1-5	4.20	0.348	0.365
1-6	2.49	0.357	0.498
2-1	6.22	0.398	0.651
2-2	16.17	0.351	0.490
2-3	8.01	0.358	0.404
2-4	3.89	0.348	0.324
3-1	15.24	0.380	0.326
3-2	4.82	0.382	0.267
3-3	8.24	0.366	0.237
3-4	3.11	0.357	0.164
3-5	0.47	0.328	

Copolymer recovery: 90%; Crude copolymer: $\overline{DS}_m$, 0.366; [η], 0.487 dl/g; Fractionation data: $\overline{DS}_m$, 0.364; [η], 0.492 dl/g

and of molecular weights ranging from 0.93 for pure PMMA to 1.4 × 10^5 for the highest $\overline{DS}_m$ (0.415).

Taking into account the efficiency of the solvent–non-solvent systems and the ease of fraction recovery (good sedimentation of the precipitated phase), we have compared 'one direction' and 'cross' fractionations for the copolymer R-19 ($\overline{DS}_m$ = 0.366, $\overline{M}_w$ = 1.43 × 10^5) selecting the following systems:

System I: $CHCl_3$ (solvent)/diethyl ether (non-solvent)

$$x_{CHCl_3,A} < x_{CHCl_3,B} \rightarrow K > 0$$

System II: DMF (solvent)/H_2O + 0.5% NH_4Cl (non-solvent)

$$\left.\begin{array}{l} x_{DMF,A} > x_{DMF,B} \\ x_{H_2O,A} > x_{H_2O,B} \end{array}\right\} \rightarrow K < 0$$

Cross system: intermediate fractions obtained by system II are further fractionated by system I.

Our experimental results are collected in *Table 1* and plotted in *Figure 2*.

For 'one direction' fractionation, system II seems slightly more efficient than system I in spite of a lower [*K*] value, probably because of its negative *K* parameter and a greater

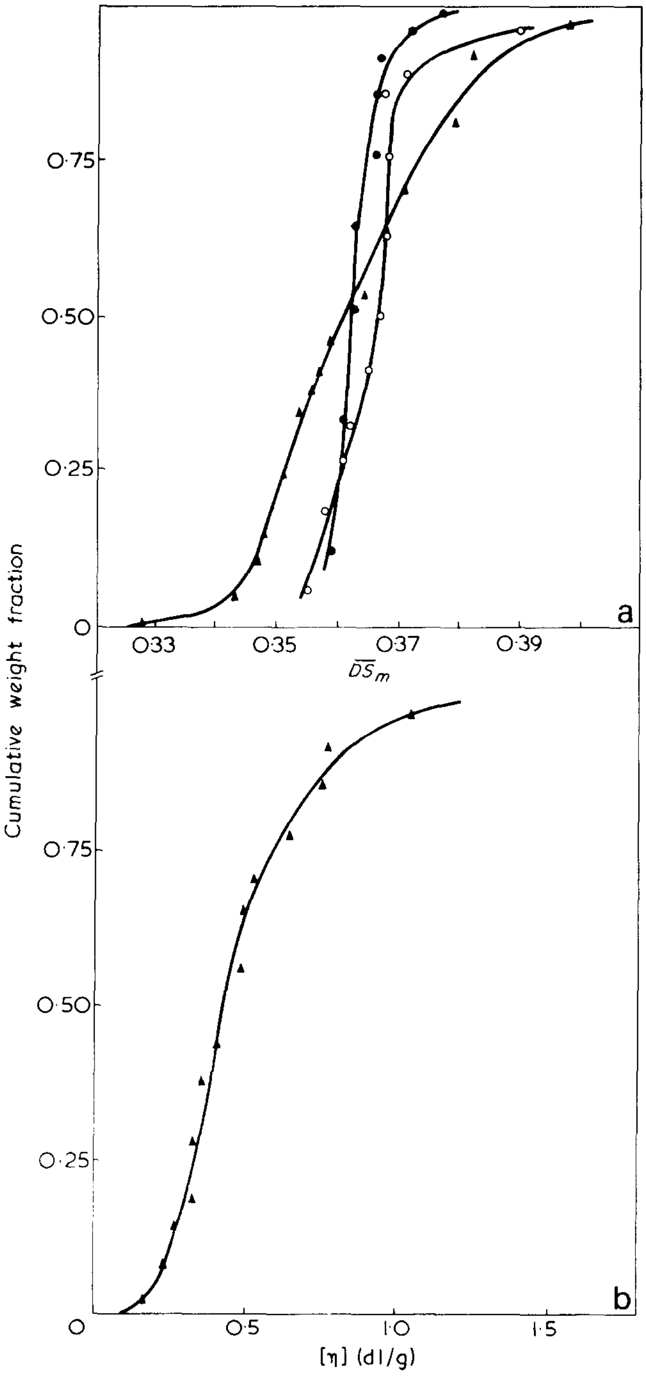


Figure 2 Fractionation of copolymer R-19. (a): Compositional distribution; ●, system I, chloroform–ethyl ether; ○, system II: DMF–water + 0.5% ammonium chloride: ▲, 'cross fractionation'; (b): intrinsic viscosity distribution

number of fractions (11 *versus* 9). The $\bar{\sigma}^2$ values of the variance, 0.9 and 6.4×10^{-5} for system I and II respectively, are very low and may be compared, especially for system I, with the apparent $\bar{\sigma}^2$ of about 0.7×10^{-5} related to a perfectly homogeneous copolymer of the same $\overline{DS}_m$ (see Experimental section). The experimental asymmetry of the compositional distribution measured by the V values (V = 1 for a symmetric distribution, see Experimental section) changes from 1.665 for system I to 0.876 for system II, and thus it has no real physical meaning. The R-19 copolymer appears quite homogeneous, when studied by 'one direction' fractionation.

'Cross' fractionation leads to a significantly higher $\bar{\sigma}^2$ value of about 2.2×10^{-4}, reflecting an actual compositional distribution which is nearly symmetrical ($V = 0.989$). This method allows the separation of an important fraction ($w_i \simeq 0.25$) of $\overline{DS}_m$ lower than 0.35, which cannot be isolated by 'one direction' fractionation. The fraction of the lowest $\overline{DS}_m$ has the lowest intrinsic viscosity; this is probably not significant, since there is no correlation between the slight fluctuations in composition and the intrinsic viscosities for the remaining 99.5% of the sample.

Thus 'cross' fractionation is clearly more efficient than 'one direction' fractionation, in good agreement with literature data related to copolymerization products[28,29]. It may be noticed that the variance $\bar{\sigma}^2$ of the R-19 sample is of the same order of magnitude as that of a radical azeotropic styrene–MMA copolymer (molar fraction of MMA = 0.497) studied by the same method[30] ($\bar{\sigma}^2 = 1.6 \times 10^{-4}$), and which appears chemically homogeneous according to 'one direction' fractionation data[31].

'One direction' fractionation of various substituted PMMA

In spite of its lower efficiency, 'one direction' fractionation remains a convenient and still reliable method for preparative purposes, provided a sufficiently sensitive solvent–non-solvent system may be found. The separation of chemically homogeneous fractions of different molecular weights but of the same composition is of interest for the study of morphological and hydrodynamical properties of the copolymers in dilute solution[1,2]. A number of substituted PMMA were fractionated, the choice of the solvent being strongly dependent on the solubility of the sample (increasing $\overline{DS}_m$ requires the use of more polar solvents). Our experimental results are collected in *Tables 2* and *3*. As pointed out previously, the dissymmetry parameters V are of little if any physical meaning, but the $\bar{\sigma}^2$ variance values are in general significant of an actual but narrow composition distribution. The lack of any important chemical heterogeneity (deviation from the average $\overline{DS}_m$ of more than 10% for a noticeable weight fraction of the copolymer, 0.1 for instance) may be reasonably ascertained. Since the $\bar{\sigma}^2$ values deduced from 'one direction' fractionation data are only underestimated values which may strongly depend on the fractionation system, the apparent increase of the variance with $\overline{DS}_m$ has not to be considered as a definitely established characteristic feature.

Study of the chemical homogeneity of substituted PMMA by light scattering

Since the pioneering work of Stockmayer *et al.*[32] and Benoit *et al.*[33], light scattering has been often used for the study of compositional homogeneity in copolymers with rather disappointing results in a number of cases[16,20]. The method[14] rests upon the analysis of the variations of the apparent experimental weight-average molecular weight $\bar{M}_w^*$ measured in different solvents according to:

$$\bar{M}_w^* = \bar{M}_w + 2P[(\upsilon_A - \upsilon_B)/\upsilon_{AB}] + Q[(\upsilon_A - \upsilon_B)/\upsilon_{AB}]^2$$

where υ_A, υ_B and υ_{AB} are the refractive index increments of homopolymer A, homopolymer B and copolymer AB respectively, $\bar{M}_w$ is the weight-average molecular weight of the copolymer; P and Q are parameters directly connected with the compositional heterogeneity of the copolymer.

We have previously checked that the υ_{AB} values of the modified PMMA are a linear function of the weight-average degree of substitution ($\overline{DS}_w$)[1–3] as expected. The relation $\upsilon_{AB} = \upsilon_A(1 - \overline{DS}_w) + \upsilon_B\overline{DS}_w$ thus allows the calculation of υ_B, which is not experimentally accessible, since quantitative substitution of radical PMMA was unsuccessful[3].

For R = $SOCH_3$, SO_2CH_3, $SO_2N(CH_3)_2$ and S C_6H_5, the υ_B values in DMF solution, at room temperature and for λ = 5460 Å, are respectively of 0.1370[1], 0.1150[3], 0.0978[3] and 0.1896[3] ml/g, while the corresponding υ_A value is 0.063 ml/g. We have thus focused our interest on the modified PMMA bearing keto-β-sulphide groups, and we have systematically studied the R-35 sample ($\bar{M}_{w\ \text{theor.}} = 1.23 \times 10^5$, $\bar{M}_{n\ \text{exp.}} = 0.85 \times 10^5$, $\overline{DS}_m = 0.307$, $\overline{DS}_w = 0.459$) in thirteen different solvents. The experimental results are collected in *Table 4*.

Linear regression analysis on the variations of the most reliable υ_A values quoted in the literature (see *Table 4*) and on the experimental υ_{AB} and calculated υ_B values *versus* the solvent refractive index n_0 leads to the following relationships.

		Regression coefficient
$t(^\circ C) = 23 \pm 2$	$\upsilon_A = 1.3677 - 0.9127\, n_0$	0.998
$\lambda = 5460$ Å	$\upsilon_B = 1.1557 - 0.6718\, n_0$	0.972
υ(ml/g)	$\upsilon_{AB} = 1.2477 - 0.7864\, n_0$	0.993

in good agreement with the empirical Gladstone–Dale equation[34].

The υ_A value in tetrahydrofurfuryl alcohol is quite close to the predicted value according to the previous relation, but υ_A in trifluoroethanol is significantly lower ($\upsilon_{\text{exp.}} = 0.1730$ *versus* $\upsilon_{\text{calc.}} = 0.1889$ ml/g) as the literature value in 2,2′, 3,3′ tetrafluoropropanol[34] ($\upsilon_{\text{exp.}} = 0.141$ *versus* $\upsilon_{\text{calc.}}$ = 0.161 ml/g).

For efficient analysis of the chemical homogeneity of copolymers, one should find copolymer–solvent systems meeting a number of important requirements, which are precisely fulfilled for the R-35 sample:

(a) $|\upsilon_A - \upsilon_B|$ sufficiently high, > 0.06 ml/g according to Spatorico[35]: its value increases from 0.121 in trifluoroethanol to 0.154 ml/g in pyridine.

(b) υ_A and υ_B both as high as possible and of the same sign, in order to determine an apparent $\bar{M}_w^*$ as close as possible to the true $\bar{M}_w$ value[36]: $\upsilon_A = 0.173$ and $\upsilon_B = 0.294$ ml/g in trifluoroethanol for instance.

(c) $\upsilon_A \cong 0$ and υ_B high, in order to allow the direct determination of the weight-average molecular weight of the B component in the AB copolymer[36]: $\upsilon_A = -0.003$ and υ_B = 0.147 ml/g in 2-methylpyridine.

(d) The copolymer itself has a sufficiently high molecular weight ($\bar{M}_{w\ \text{theor.}} = 1.23 \times 10^5$) and degree of substitution ($\overline{DS}_w = 0.459$), in order to avoid any trouble from a possible

Table 2a 'One direction' fractionation for copolymer R-12 substituted PMMA [R = $SO_2N(CH_3)_2$]

Fraction no	Weight fraction, $w_i \times 10^2$	DS_m^i	$[\eta]$ (dl/g)	$\overline{M}_w \times 10^{-5}$
1	7.80	0.148	0.690	2.36
2	9.65	0.148	0.675	2.13
3	9.65	0.145	0.630	2.04
4	6.68	0.146	0.560	1.87
5	17.83	0.141	0.545	1.59
6	10.39	0.144	0.465	1.36
7	9.72	0.147	0.415	1.22
8	10.39	0.140	0.365	0.94
9	12.62	0.142	0.285	0.88
10	5.27	0.147	0.161	0.36

90% Copolymer recovery

	$\overline{DS}_m$	$[\eta]$ (dl/g)	$\overline{M}_w \times 10^{-5}$
Crude copolymer	0.142	0.450	1.37
Fractionation data	0.144	0.485	1.48

Table 2b 'One direction' fractionation for copolymer R-16 substituted PMMA [R = $SO_2N(CH_3)_2$]

Fraction no	Weight fraction, $w_i \times 10^2$	DS_m^i	$[\eta]$ (dl/g)	$\overline{M}_w \times 10^{-5}$
1	8.09	0.252	0.815	2.59
2	13.87	0.247	0.705	2.26
3	10.26	0.236	0.627	1.93
4	13.58	0.250	0.549	1.70
5	16.11	0.231	0.490	1.36
6	13.15	0.238	0.420	1.10
7	12.35	0.239	0.305	0.80
8	5.49	0.238	0.240	0.545
9	7.08	0.237	0.154	0.31

92% Copolymer recovery

	$\overline{DS}_m$	$[\eta]$ (dl/g)	$\overline{M}_w \times 10^{-5}$
Crude copolymer	0.240	0.470	1.38
Fractionation data	0.241	0.498	1.46

Table 2c 'One direction' fractionation for copolymer R-3 substituted PMMA [R = $SO_2N(CH_3)_2$]

Fraction no	Weight fraction, $w_i \times 10^2$	DS_m^i	$[\eta]$ (dl/g)	$\overline{M}_w \times 10^{-5}$
1	12.99	0.382	0.810	2.18
2	7.37	0.380	0.765	1.98
3	9.81	0.389	0.575	1.37
4	3.35	0.388	0.523	1.33
5	15.09	0.390		
6	6.79	0.390	0.445	1.03
7	10.06	0.388	0.385	0.81
8	5.87	0.386	0.380	0.79
9	6.37	0.405	0.272	0.56
10	3.35	0.386	0.265	0.535
11	5.03	0.385	0.240	0.45
12	6.54	0.379		
13	3.52	0.400	0.175	0.305
14	3.86	0.406		

91% Copolymer recovery

	$\overline{DS}_m$	$[\eta]$ (dl/g)	$\overline{M}_w \times 10^{-5}$
Crude copolymer	0.395	0.525	1.12
Fractionation data	0.388	0.478	1.14

Table 2d 'One direction' fractionation for copolymer R-10 substituted PMMA [R = $SO_2N(CH_3)_2$]

Fraction no	Weight fraction, $w_i \times 10^2$	DS_m^i	$[\eta]$ (dl/g)
1	2.00	0.743	0.950
2	3.86	0.729	0.800
3	2.21	0.795	0.700
4	3.81	0.753	
5	14.44	0.778	0.680
6	10.70	0.747	0.650
7	3.45	0.729	0.600
8	11.32	0.784	0.550
9	13.53	0.770	0.480
10	11.88	0.764	0.375
11	6.06	0.791	0.332
12	9.67	0.786	0.295
13	2.80	0.770	0.220

85% Copolymer recovery

	$\overline{DS}_m$	$[\eta]$ (dl/g)
Crude copolymer	0.755	0.527
Fractionation data	0.769	0.515

Table 2e 'One direction' fractionation of copolymer R-22 substituted PMMA [R = SO_2CH_3]

Fraction no	Weight fraction, $w_i \times 10^2$	DS_m^i	$[\eta]$ (dl/g)	$\overline{M}_w \times 10^{-5}$
1	15.28	0.312	1.250	3.57
2	11.22	0.317	0.880	2.30
3	9.96	0.302	0.754	1.98
4	4.42	0.300	0.687	1.76
5	8.62	0.319	0.670	1.58
6	13.32	0.309	0.480	1.26
7	10.52	0.305	0.395	0.90,5
8	3.58	0.332	0.390	0.80
9	7.43	0.295	0.315	0.66
10	10.52	0.298	0.268	0.52
11	5.12	0.308	0.195	0.33 5

90% Copolymer recovery

	$\overline{DS}_m$	$[\eta]$ (dl/g)	$\overline{M}_w \times 10^{-5}$
Crude copolymer	0.299	0.615	1.45
Fractionation data	0.308	0.634	1.62

dependence of υ_A and υ_B on molecular weights of A and B components in the copolymer[37].

Among the twelve solvents tested eleven solvents, covering a wide range of υ_{AB} values from 0.228 in trifluoroethanol to 0.059 ml/g in pyridine, lead to a remarkably constant $\overline{M}_w^*$ value of (1.35 ± 0.04) x 10^5, quite close to the theoretical $\overline{M}_w$ (1.23 ± 0.07) x 10^5 calculated from the corresponding values of the molecular weight of the PMMA precursor and of the substitution degree. The higher $\overline{M}_w^*$ value determined in toluene, 1.72 x 10^5, may be discarded, since aggregation does occur in this solvent at room temperature (the second virial coefficient is negative, and the intensity of the scattered light is exceedingly sensitive to small variations of temperature). Our copolymer sample thus appears chemically homogeneous, but at the limit of the sensitivity of the method. In particular we were not able to find suitable solvents of high refractive indexes (low values of υ_{AB}), where $\overline{M}_w^*$ is the most sensitive to slight fluctuations in composition in the copolymer: aggregation is by far more important in

Table 3 Fractionation data on substituted PMMA bearing keto-β-functional groups $COCH_2R$

Run	R	Conditions of synthesis	$\overline{DS}_m$	Fractionation system	$\bar{\sigma}^2 \times 10^5$	V
R-12	$SO_2N(CH_3)_2$	THF, heterogeneous phase	0.142	$CHCl_3$/petroleum ether	0.9	0.96
R-16	$SO_2N(CH_3)_2$	THF, heterogeneous phase	0.240	$CHCl_3$/petroleum ether	4.9	1.66
			0.366	$CHCl_3$/ethyl ether (system I)	0.9	1.67
R-19	$SO_2N(CH_3)_2$	THF, heterogeneous phase	0.366	DMF/H_2O + 0.5%NH_4Cl (system II)	6.4	0.88
			0.366	'Cross fractionation'	22	0.99
R-3	$SO_2N(CH_3)_2$	THF + HMPA, homogeneous phase	0.395	Acetone/petroleum ether	4.9	1.08
R-10	$SO_2N(CH_3)_2$	THF + HMPA, homogeneous phase	0.760	DMF/ethyl ether	31	0.62
A-3	$SOCH_3$	DMSO, homogeneous phase	0.289	$CHCl_3$/petroleum ether	3.8	0.62
R-22	SO_2CH_3	THF + DMSO, homogeneous phase	0.299	Acetone + MeOH (1 vol:1vol)/MeOH	6.4	0.89

Table 4 Light scattering study of copolymer R-35 (R = SC_6H_5, $\overline{DS}_m$ = 0.307)

Solvent	$n_{0\ 5460Å}^{25°C}$ [a]	Refractive index increments (ml/g)			$\bar{M}_w^* \times 10^{-5}$
		υ_A	υ_B	υ_{AB}	
Trifluoroethanol	1.2905	0.1730	0.2938	0.2285	1.32
Acetone	1.3581	0.1321[c]	0.2494	0.1860	1.43
Ethyl acetate	1.3715	0.1180[c]	0.2407	0.1744	1.41
Tetrahydrofuran	1.4066	0.0870[c]	0.2162	0.1464	1.34
Dioxane	1.4218	0.0696[c]	0.1858	0.1230	1.39
Dimethylformamide	1.4334	0.0630[c]	0.1896	0.1212	1.21
Chloroform	1.4446	0.0616[c]	0.1876	0.1195	1.32
Tetrahydrofurfuryl alcohol	1.4499[b]	0.0440	0.1613	0.0979	1.42
N-Methylpyrrolidone	1.4680[b]	0.0176[c]	0.1675	0.0865	1.36
Toluene	1.4980	0.0004[d]	0.1544	0.0712	1,72[e]
2-Methylpyridine	1.5023	−0.0035[d]	0.1466	0.0655	1.34
Pyridine	1.5115	−0.0119[d]	0.1426	0.0591	1.37
Chlorobenzene	1.5239	−0.0260[c]	0.1530	0.0563	

[a] Johnson, B. L. and Smith, H. in 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, London, 1972 p 27

[b] $n_D^{25°C}$, Organic Solvents, Riddick, J. A. and Bunger, W. B., Wiley Interscience, New York, 1970

[c] Huglin, M. B. in 'Polymer Handbook', (Ed. J. Brandrup and E. H. Immergut), 2nd edn, Wiley Interscience, New York, 1975, IV-267

[d] Extrapolated values

[e] Second virial coefficient is negative, and the polymer solution is aggregated

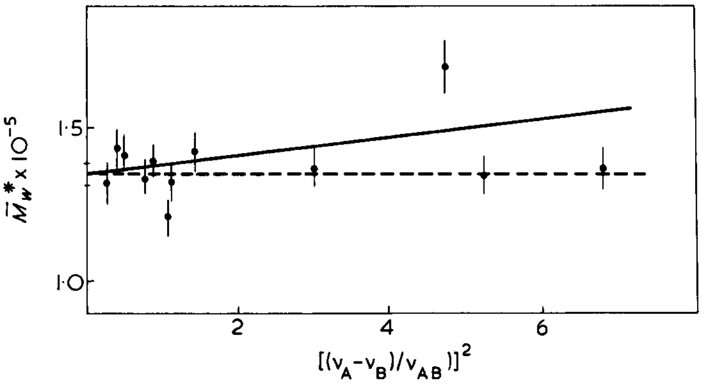


Figure 3 Variations of the apparent molecular weight $\bar{M}_w^*$ of copolymer R-35 in various solvents. – – – –, Experimental regression line; ———, calculated line for $\bar{\sigma}^2 = 2.2 \times 10^{-2}$

solvents like chlorobenzene (υ_{AB} = 0.056 ml/g) for instance.

Since for copolymers of sufficient chain length obtained by chemical modification of a homopolymer precursor there is no correlation between the fluctuations in composition and the molecular weight (as we have previously checked by fractionation), the variations of $\bar{M}_w^*$ may be merely described according to[20]:

$$\bar{M}_w^* = \bar{M}_w + Q[(\upsilon_A - \upsilon_B)/\upsilon_{AB}]^2, \text{ with } Q = \bar{\sigma}^2 \times \bar{M}_w$$

Regression analysis on the variations of our experimental $\bar{M}_w^*$ values *versus* $[(\upsilon_A - \upsilon_B)/\upsilon_{AB}]^2$ (*Figure 3*) leads to the relation (R = 0.994):

$$\bar{M}_w^* = 1.356 \times 10^5 - 1.696[(\upsilon_A - \upsilon_B)/\upsilon_{AB}]^2$$

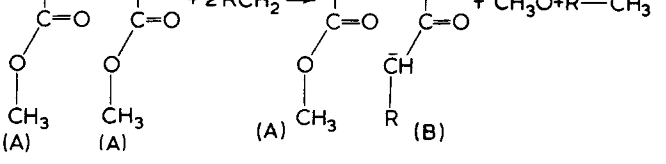
The negative Q value has no physical meaning, and it merely reflects the fact that the $\bar{M}_w^*$ fluctuations are within the experimental accuracy. Assuming that a difference of about 15% between $\bar{M}_w^*$ and $\bar{M}_w$ in the most sensitive solvent (υ_{AB} minimum = 0.059 ml/g in pyridine) is high enough to be significant of an actual compositional heterogeneity, one may evaluate the lowest limit of heterogeneity which may be detected. For the R-35 sample, we have found: $\bar{\sigma}^2 = Q/\bar{M}_w < 2.2 \times 10^{-2}$, i.e. about 8.8% of the maximum value of $Q/\bar{M}_w$ (0.25 for an equal weight mixture of homopolymers A and B).

In spite of a number of favourable parameters in our case, light scattering study of compositional homogeneity remains a rather poorly sensitive method, because of a yet too narrow range of υ_{AB} values easily available, and of a too low value of the molecular weight of the copolymer sample[38].

Correlation between chemical homogeneity of the substituted PMMA and characteristic features of their preparation

The chemical homogeneity of copolymers obtained by modification of a polymeric substrate is a complex function of the molecular characteristics of the precursor ($\overline{DP}_n$ and *MWD*), of the extent of substitution ($\overline{DS}_m$) and of the reaction kinetics. For sufficiently long chains, the influence of the molecular weight distribution becomes negligible; quantitative correlations between chemical homogeneity and $\overline{DP}_n$, $\overline{DS}_m$ and the kinetic parameters have been theoretically derived, by both Monte Carlo simulations[39] and analytical calculations using Markovian approximations[4,40,41]. Assuming that the substitution kinetics may be completely described by the three rate constants k_0, k_1 and k_2 related to the reaction site $\overset{*}{\mathrm{A}}$ in its three chemically different environments ($\mathrm{A\overset{*}{A}A}$, $\mathrm{A\overset{*}{A}B}$ and $\mathrm{B\overset{*}{A}B}$ respectively) it has been shown that the chemical homogeneity of the copolymer increases with the precursor $\overline{DP}_n$ and is strongly dependent on substitution kinetics: autoaccelerated kinetics ($k_0 < k_1 < k_2$) leads to drastic enhancements of the chemical heterogeneity, in sharp contrast with simple kinetics without any neighbouring group effects ($k_0 = k_1 = k_2$), and even more with autoretarded kinetics ($k_0 < k_1 < k_2$) which gives the highest chemical homogeneity.

The experimental results collected in *Table 3* clearly show that the substituted PMMA are all characterized by a fairly high chemical homogeneity over the whole range of $\overline{DS}_m$ investigated ($\overline{DS}_m < 0.76$), whatever the reaction conditions are: homogeneous solution, when both the organolithium reagent and the modified polymer are soluble in the reaction medium ($CH_3SO_xCH_2Li$, with $x = 1$ or 2, in presence of DMSO and $(CH_3)_2NSO_2CH_2Li$ in presence of HMPA); heterogeneous solution, when the modified polymer precipitates out of the solution as soon as the substitution degree reaches a critical value of about 0.20 ($C_6H_5SCH_2Li$ and $(CH_3)_2NSO_2CH_2Li$ in THF). The substitution process is characterized by autoretarded kinetics, as a result of increasing steric hindrance and electrostatic repulsion between the reagent RCH_2^- and the polycarbanionic chain[1–3]:



$$k_0(\mathrm{A\overset{*}{A}A}) > k_1(\mathrm{B\overset{*}{A}A}) > k_2(\mathrm{B\overset{*}{A}B})$$

Thus the fairly high chemical homogeneity of the substituted PMMA may be readily taken into account by the conjugated effects of the high molecular weight of the polymeric precursor ($\overline{DP}_n = 700$) and the autoretarded kinetics. Precipitation of the modified chain, when the reaction is carried out without a strongly dipolar aprotic solvent like DMSO or HMPA, is thought to be a favourable factor increasing chemical homogeneity of the copolymer. The solubility of the carbanionic chain is much more dependent on its $\overline{DS}_m$ than on its $\bar{M}_w$, and the heterogeneous reaction on an insoluble highly modified chain is clearly strongly decreased with respect to the reaction on a soluble but less modified chain.

Quantitative correlations between the experimental $\bar{\sigma}^2$ values and kinetic parameters are out of the scope of the present study. However the copolymer R-35 bearing keto-β-sulphonamide groups ($\overline{DS}_m = 0.366$) may deserve special interest, since 'cross' fractionation allows the determination of a reliable $\bar{\sigma}^2$ value. Assuming that the reaction proceeds without any neighbouring group effects, a maximum $\bar{\sigma}^2$ value of about 3.1×10^{-4} may be evaluated both from the chart given by Plate *et al.*[40,41] and from the relationship derived by Frensdorff *et al.*[4]: $[\bar{\sigma}^2 = \overline{DP}_n{}^{-1} \times (\overline{DS}_m - \overline{DS}_m^2)]$ On the other hand, autoretarded kinetics with characteristic ratios $k = k_1/k_0 \simeq 0.2$ and $k' = k_2/k_0 \simeq 0$, as measured in homogeneous solution[42], would lead to a maximum $\bar{\sigma}^2$ value of about 1×10^{-4}, as deduced from the chart of Plate *et al.*[40,41], assuming that variations of $\bar{\sigma}^2$ *versus* $\overline{DS}_m$ may be neglected within the narrow range $0.366 < \overline{DS}_m < 0.5$. The experimental $\bar{\sigma}^2$ value of about 2.2×10^{-4} is just between the two calculated values, and it would be misleading to hope for better agreement with either of them, taking into account the previous assumptions and the accuracy of the $\bar{\sigma}^2$ experimental value. Thus, for the high molecular weight copolymer investigated in this study, the observed compositional heterogeneity is in good agreement with the autoretarded kinetics of the substitution process.

However, it does not seem possible to estimate quantitatively the respective contributions of the molecular weight and of the autoretarded kinetics to the narrowing of the composition distribution. The study of chemical homogeneity is not sufficient to ascertain unambiguously the kinetic characteristics, which have to be studied independently. The recent work of Plate *et al.*[43] on the autoretarded quaternization of poly(4-vinylpyridine) by benzylchloride in homogeneous solution has to be pointed out: a single set of constants k_0: k_1: k_2 = 1: 0.3: 0.3 does allow a perfect agreement between experimental data and theoretical values for both kinetics and compositional distribution.

CONCLUSION

The ketonic-β-functionalized copolymers derived from PMMA by nucleophilic substitution of primary stabilized organolithium reagents retain the molecular characteristics of the precursor ($\overline{DP}_n$, *MWD* and tacticity), and show fairly high chemical homogeneity over a wide range of compositions. This important feature, which may be correlated with both the high molecular weight of the polymeric precursor and the characteristic autoretarded kinetics of the reaction process, points out the interest of chemical modification of polymers as a preparative method of well defined random copolymers, since for copolymerization reaction products the compositional heterogeneity is narrow and well ascertained only in a few cases, such as azeotropic copolymerization.

ACKNOWLEDGEMENTS

The authors are greatly indebted to Mr Gueguen for carrying out most of the tedious fractionation labour. They wish to acknowledge Dr Rempp for his constant interest in this study, and critical review of the manuscript. This work was partly supported by the Delegation Generale a la Recherche Scientifique et Technique (contracts 71.7.2896 and 73.7.1130).

REFERENCES

1 Arranz, F. and Galin, J. C. *Makromol. Chem.* 1972, **152**, 185
2 Bourguignon, J. J., Roussel, R., Spegt, P. and Galin, J. C. 4th *Bratislava Prepr. IUPAC Int. Conf. Modified Polymers, their preparation and properties* 1975, **1**, 9
3 Bourguignon, J. J. and Galin, J. C. *Macromolecules* in press
4 Frensdorff, H. K. and Ekiner, O. *J. Polym. Sci (A-2)* 1967, **5**, 1157
5 Plate, N. A. in 'IUPAC Symposium on Macromolecular Chemistry', Akademiaii Kiado, Budapest 1971, p 651
6 Klesper, E., Strasilla, D. and Barth, V. in 'Reactions on Polymers, D. Reidel, Dortrecht, Holland, 1973, p 137
7 Plate, N. A. in 'Reactions on Polymers', (Ed. J. A. Moore) D. Reidel, Dortrecht, Holland, 1973, p 169

8 Plate, N. A., *Pure Appl. Chem.* 1976, **46**, 49

9 Guzman, G. M. in 'Progress in High Polymers', (Eds J. C. Robb and F. W. Peaker), Heywood, London, 1961, p 113

10 Fuchs, O. and Schneider, W. in 'Polymer Fractionation', (Ed. M. J. R. Cantow), Academic Press, New York, 1967, p 341

11 Fuchs, O. *Angew. Makromol. Chem.* 1973, **33**, 1

12 Hermans, J. J. and Ende, H. A. in 'Newer Methods of Polymer Characterization', (Ed B. Ke), Interscience, New York, 1964, p 525

13 Nakasawa, A. and Hermans, J. *J. Polym. Sci. (A-2)* 1971, **9**, 1871

14 Benoit, H. and Froelich, D. in 'Light Scattering from Polymer Solutions', (Ed. M. G. Huglin), Academic Press, London, 1972, p 467

15 Tung, L. H. *J. Macromol. Sci. (C)* 1971, **6**, 51

16 Grubisic-Gallot, Z., Picot, M., Gramain, Ph. and Benoit, H. *J. Appl. Polym. Sci.* 1972, **16**, 2931

17 Inagaki, H., Matsuda, H. and Kamiyama, F. *Macromolecules* 1968, **1**, 520

18 Kamiyama, F., Matsuda, H. and Inagaki, H. *Makromol. Chem.* 1969, **125**, 286

19 Teramachi, S. and Esaki, H. *Polym. J.* 1975, **7**, 593

20 Lamprecht, J., Strazielle, C., Dayantis, J. and Benoit, H. *Makromol. Chem.* 1971, **148**, 285

21 Rosenthal, A. J. and White, B. B. *Ind. Eng. Chem.* 1952, **44**, 2693

22 Cantow, H. J. and Fuchs, O. *Makromol. Chem.* 1965, **83**, 244

23 Topchiev, A. V., Litmanovitch, A. D. and Shtern, Y. Ya. *Dokl. Akad. Nauk. USSR* 1962, **147**, 1389

24 Teramachi, S. and Nagasawa, M. *J. Macromol. Sci. (A)* 1968, **2**, 1169

25 Glöckner, G., *Eur. Polym. J. (Suppl)*, 1969, p 463

26 Litmanovitch, A. D. and Shtern, Y. *J. Polym. Sci. (C)* 1967, 1375

27 Kudryavtseva, L. G. and Litmanovitch, A. D. *Polym. Sci. USSR* 1967, **9**, 1132

28 Teramachi, S. and Kato, Y. *J. Macromol. Sci. (A)* 1970, **4**, 1875

29 Teramachi, S. and Fukao, T. *Polym. J.* 1974, **6**, 532

30 Teramachi, S. and Kato, Y. *Macromolecules* 1971, **4**, 54

31 Lovric, L. J., Grubisic-Gallot, Z. and Kunst, B. *Eur. Polym. J.* 1976, **12**, 189

32 Stockmayer, W. H., Moore, Jr., L. D., Fixman, M. and Epstein, B. N. *J. Polym. Sci.* 1953, **16**, 517

33 Bushuk, W. and Benoit, H. *Can. J. Chem.* 1958, **36**, 1616

34 Huglin, M. B. in 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, London, 1972, p 165

35 Spatorico, A. L. *J. Appl. Polym. Sci.* 1974, **18**, 1793

36 Tuzar, Z., Kratochvil, P. and Strakova, D. *Eur. Polym. J.*, 1970, **6**, 1113

37 Chau, T. C. and Rudin, A. *Polymer* 1974, **15**, 593

38 Vorlicek, J. and Kratochvil, P. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 855

39 Plate, N. A., Litmanovitch, A. D., Noa, O. V. and Golyakov, V. I. *Polym. Sci. USSR* 1969, **11**, 2511; *Eur. Polym. J. (Suppl)* 1969, p 517

40 Noah, O. V., Litmanovitch, A. D. and Plate, N. A. *J. Polym. Sci. (Polym. Phys. Edn)* 1974, **12**, 1711

41 Noah, O. V., Toom, A. L., Vasiliv, N. B., Litmanovitch, A. D. and Plate, N. A. *Polym. Sci. USSR* 1974, **16**, 480

42 Bourguignon, J. J. and Galin, J. C. unpublished results

43 Noah, O. V., Torchilin V. P., Litmanovitch, A. D. and Plate, N. A. *Polym. Sci. USSR* 1974, **16**, 775