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Plasma-Induced Living Radical Copolymerization

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ABSTRACT

Plasma-induced polymerization (copolymerization) is a new method of polymer synthesis. Different comonomer pairs (methyl methacrylate-styrene, methyl methacrylate-α-methylstyrene, acrylonitrile-α-methylstyrene, methacrylonitrile-styrene, butyl methacrylate-styrene) have been copolymerized by this technique. The results showed that the process proceeds through a living radical mechanism and yields ultrahigh molecular weight macromolecular compounds (pleistomers). So, the reactivity ratio values of the monomers copolymerized by this technique are very close to those yielded by their classical radical copolymerization, and the microstructure of the copolymers is similar to that of their radically obtained homologs. Some characteristics, as well as some solution properties, of the ultrahigh molecular weight copolymers obtained are also presented.

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INTRODUCTION

Plasma-induced polymerization (copolymerization) is a new method of polymer synthesis. In this particular case the initiation reaction takes place in the gaseous phase and the formation of low molecular weight active species, able to act as propagation centers, is (practically) instantaneous. The molecular weight and polydispersity of the resulting polymers are directly related to the reaction conditions, and the activity of the propagating chains appears to be unusually high and very stable over time, even at room temperature. The polymerization (copolymerization) reactions performed according to this technique yield very high or ultrahigh molecular weight polymers (copolymers) and occur at room temperature.

Based on a series of published papers [1-5], the plasma-induced polymerization method appears to be different from all classical polymerization techniques, as well as from plasma polymerization. The latter method generally produces highly crosslinked, amorphous polymers, thus differing considerably from the conventional ones.

The first part of the present paper is concerned with different plasma-induced copolymerization reactions, performed to establish the mechanism of the process and its specific features. The last part presents some characteristics of the ultrahigh molecular weight copolymers obtained, e.g., molecular weight and compositional polydispersity (heterogeneity). Some data on solution properties are also reported.

EXPERIMENTAL

Polymerization Technique

The general experimental procedure is described in previously published papers [3-5]. Typically, the monomers were purified with great care and then introduced in polymerization ampules, frozen in liquid nitrogen after degassing, evacuated repeatedly to 10^{-3} to 10^{-4} torr, and sealed. An electrical discharge was then operated between two external electrodes, situated at about 2.5 and 7.0 cm, respectively, from the frozen comonomer mixture. Both electrodes were coupled to a high frequency discharge generator (frequency, 2.5 MHz; power, 100 W). A third electrode, unconnected to the power source, was placed at about 1.0 cm from the sample in order to restrict the discharge and to impede it from touching the frozen sample. The discharges were operated for 20 to 300 s. The ampules were kept in the dark, at room temperature, for different periods of time (postpolymerization period), and then opened to separate the copolymer.

All copolymerization reactions performed to determine the reactivity ratio values of the comonomers were stopped at conversions of less than 10%.

Separation of the Copolymers

The copolymers were separated by diluting the contents of the ampules with large amounts of solvents and precipitating in nonsolvents. All macromolecular compounds synthesized through this technique proved to be completely soluble, in specific solvents over time.

In order to prevent shear degradation, no mechanical stirring was applied to the polymer solutions at any stage.

Copolymerization Systems

The following copolymerization systems were considered:

Methyl methacrylate (MMA, M_1)-styrene (S, M_2)
MMA (M_1)-α-methyl styrene (MS, M_2)
Acrylonitrile (AN, M_1)-MS (M_2)
Methacrylonitrile (MAN, M_1)-S (M_2)
Butyl methacrylate (BuMA, M_1)-S (M_2)

These systems were selected from among those most studied in order to compare the data obtained by plasma-induced copolymerization with that of conventional copolymerization reactions.

Characterization of the Copolymers

^{1}H-NMR spectroscopy was used to determine the composition of the copolymers. The spectra were registered on a Jeol C-60 HL spectrometer operating at 60 MHz.

For MMA-S and MMA-MS copolymers, the splitting of the methoxy signal in ^{1}H-NMR spectra allowed the determination of the probability of alternating coisotactic addition, σ. For MAN-S copolymers, α-methyl signal splitting was used for the same purpose.

Copolymerization data were processed by the Kelen-Tüdős method.

Weight-average molecular weights ($\overline{M}_w$) were obtained from light-scattering measurements performed on a PCL Peaker apparatus in different solvents. Number-average molecular weights ($\overline{M}_n$) were calculated from light-scattering data determined in theta solvents, using the Debye theory, by considering the particle scattering function of a molecular-weight polydisperse sample of a linear flexible polymer in the unperturbed state [6].

Compositional heterogeneity of the copolymers was evaluated from light-scattering data.

RESULTS AND DISCUSSION

Reactivity Ratio Values and Microstructural Aspects

Table 1 presents the reactivity ratio and σ-values for the systems studied.

In all cases the Kelen-Tüdös plots proved to be straight lines, thus indicating that the terminal model of copolymerization characterizes the systems. Literature data [7] show that, during propagation, the MMA-MS and AN-MS systems present depolymerization reactions which have to be taken into account, especially at elevated temperature. However, because plasma-induced copolymerization is performed at room temperature, the depolymerization reactions can be neglected.

The value of $\sigma = 0.21$ for the MMA-MS system indicates a rather high cosindiotactic preference for alternating addition. Izu et al. [8] established the σ-value dependence on copolymerization between 60 and 147°C for this system. The value found at 22°C agrees with their Arrhenius plot, confirming that the terminal model of copolymerization properly describes the system at this temperature.

In the case of the AN-MS system, both the copolymerization diagram and the Kelen-Tüdös plot confirm the strong tendency of the two comonomers to alternate.

The value of $\sigma = 0.48$ for the MMA-S system is in the range of value previously found for the radical copolymerization of the two comonomers [9].

The σ-value of the MAN-S system is rather high, and indicates a strong tendency for coisotacticity of phenyl and α-methyl groups.

For all the copolymerization pairs studied, both the reactivity ratio values and the configurational parameters are similar to those reported for the classical radical copolymerization of the same systems. In addition, the presence of radical polymerization inhibitors impedes

TABLE 1. Reactivity Ratio and σ-Values of the Systems Studied

M_1-M_2 system	r_1	r_2	σ
MMA-S	0.41	0.57	0.48
MMA-MS	0.42	0.22	0.21
AN-MS	0.03	0.14	
MAN-S	0.21	0.34	1.00
BuMA-S	0.59	0.74	

formation of the copolymers, so it appears that plasma-induced copolymerization proceeds via a free radical mechanism.

Mechanism of Plasma-Induced Copolymerization

The mechanism of plasma-induced polymerization (copolymerization) was previously proved to be by living radicals [10, 11]. The existing macroradicals have been used as macromolecular initiators [12] for the synthesis of block copolymers. A kinetic model of this unterminated polymerization reaction, with instantaneous initiation, has recently been published [13].

Molecular Weight and Polydispersity Data

For long postpolymerization periods, the plasma-induced copolymerization technique yields very high or ultrahigh molecular weight copolymers. Due to the specific problems associated with the study of these ultralong macromolecular chains and with their characteristics, which are different from those of the usual polymers, the term "pleistomers" (pleistos = very many, so "very many mers") is proposed.

Table 2 presents some molecular weight and polydispersity data on poly(methyl methacrylate-co-styrene) 50:50 mol/mol samples obtained by this technique. The initial monomer mixture was calculated

TABLE 2. Molecular Weight and Polydispersity Data on Poly(Methyl Methacrylate-co-Styrene) (MMA-S 50:50 mol/mol) Samples Obtained by Plasma-Induced Copolymerization

Sample	Postpolymerization period, h	Yield, %	$\overline{M}_w \times 10^{-6}$ D[a]	$\overline{M}_w \times 10^{-6}$ EMK[a]	$\overline{M}_w \times 10^{-6}$ C[a]	$\overline{M}_n \times 10^{-6}$ C[a]
1	120	0.52	7.3	7.3		
2	280	1.04	18.4	17.9	18.3[b]	11.3[b]
3	480	1.15	20.4	20.2		
4	640	1.73	36.8	39.5	37.3[c]	24.9[c]
5	1003	2.41	55.3	57.7		
6	1143	2.60	67.6	66.0		

[a] D = 1,4-dioxane, 20°C; EMK = ethyl methyl ketone, 20°C; C = cyclohexanol (theta solvent, 68.6°C, according to Ref. 15).

[b] $\overline{M}_w/\overline{M}_n = 1.62$.

[c] $\overline{M}_w/\overline{M}_n = 1.49$.

to yield a copolymer of 50:50 (mol/mol) composition according to the established reactivity ratio values of the monomers.

The data show that ultrahigh molecular weight polymers have been obtained. For the same samples, only differences within the limits of experimental error are noted for the molecular weights determined in the three solvents. The copolymerization yields are very low, so it is concluded that the copolymers have very small compositional heterogeneity. The same conclusion was reached from a study of MAN-S copolymers [14].

Problems Associated with the Investigation of Solution Properties of Pleistomers

A number of problems are associated with investigations of the properties of pleistomers [16-18]. Most techniques for the determination of molecular weights and their distribution have been restricted and verified for molecular weights of less than 5×10^6. Extension of the molecular weight scale might provide an experimental test for many theoretical equations.

It is even more difficult to evaluate and discuss other characteristic parameters of the macromolecular chain, e.g., the heterogeneity, the perturbed and unperturbed dimensions, and the excluded volume. In other words, equations based on the two-parameter theory, where the second virial coefficient A_2 and the expansion factor α_s are functions of short- and long-range interactions, will have to be modified for the correct characterization and interpretation of the experimental data.

To give an example of the problems, Fujita et al. [19, 20] reported some anomalies in the interpretation of the interpenetration function, Ψ. The anomalies appear mainly as a consequence of the modification of the dependence between A_2 and the molecular weight in the ultrahigh molecular weight region.

The excluded-volume effect in dilute polymer solutions is generally discussed in terms of the expansion factor α_s and the interpenetration function Ψ, defined as the degree of penetration of polymer chains in dilute solution. The interpenetration function, defined by

$$\Psi(Z) = A_2 M^2/(4\pi^{3/2} N_A \langle S^2 \rangle^{3/2}) \qquad (1)$$

is a function of the excluded volume parameter, Z.

There are only a limited number of approaches, based on experimental data, for discussing the asymptotic solutions of $\Psi(Z)$ for high values of $\overline{Z}$ (where $\overline{Z} = Z/\alpha_s^3$). For ultrahigh molecular weight polymers, based on physical considerations, polymer molecules with $Z \to \infty$ tend to become rigid spheres in dilute solutions, so that $\Psi(Z)$ becomes a constant independent of Z.

The use of the light-scattering technique for the study of pleistomers requires a search for new methods of characterization, starting from theoretical considerations that have been verified for polymers of the usual length.

Generally, light-scattering measurements use solutions of about 0.01 g/cm^3, depending on the molecular weight of the sample and on the refraction index of the solvent; the lower concentration limit is easily established. For ultrahigh molecular weights, the concentration range is not available. Extrapolation of the experimental curves to evaluate the $\overline{M}_w$ values, the radii of gyration, or the second virial coefficients requires consideration of the experimental data obtained for diffusion angles up to 45° and for very low concentration ranges, e.g., for poly(methyl methacrylate) in CCl_4 at 27°C, the concentration range was 10^{-4} to 7×10^{-4} g/cm^3. With a decrease of concentration, the range of diffusion angles where $(Kc/R_\theta)^{1/2}$ varies linearly with $\sin^2 (\theta/2)$ becomes narrower. Generally speaking, the concentration range to be used for pleistomers is much lower, and, as a consequence, a more pronounced curvature appears for $(Kc/R_\theta)^{1/2}_{c=0}$ - $\sin^2 (\theta/2)$ dependence (Fig. 1).

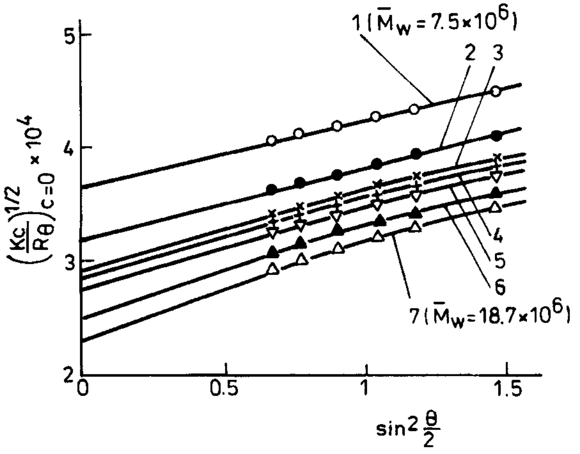

FIG. 1. Reciprocal square root of reduced scattering intensity at zero concentration as a function of $\sin^2 (\theta/2)$ for poly(methyl methacrylate) samples in CCl_4 at 27°C (theta solvent). Curves 2-6 are for intermediate molecular weight values.

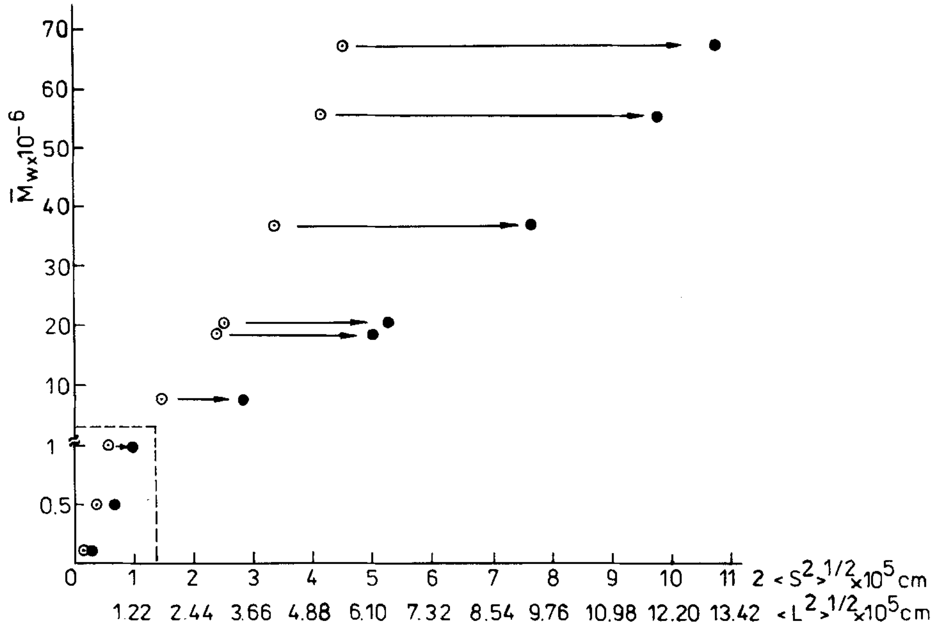

FIG. 2. Dependence of diameter $(2\langle S^2\rangle^{1/2})$ and of end-to-end distance $(\langle L^2\rangle^{1/2})$ of MMA-S 50:50 random copolymers on the molecular weight in (○) cyclohexanol at 68.6°C and (●) 1,4-dioxane. The broken line indicates the generally studied molecular weight domain.

The lower concentration limit of solutions to be used for the correct interpretation of experimental data is a function of the molecular weight of the sample under study. Thus, for MMA-S 50:50 mol/mol random copolymers, macromolecular chains up to $\overline{M}_w = 67.6 \times 10^6$ were obtained; the particles representing them exceed 1 μm in diameter, and the end-to-end distances of the macromolecules reach up to 1.3 μm (Fig. 2).

The size of the polymers generally studied ($\overline{M}_w \leq 5 \times 10^6$) is of the same order of magnitude as the wavelength of the unpolarized light used in the light-scattering technique. In the case of pleistomers, the size is much larger, so that the classically established particle-scattering factor can lead to erroneous results.

The determination of the molecular weight heterogeneity of pleistomers was performed by using light-scattering data obtained in theta solvents according to the simplified equation established for high molecular weights and large diffusion angles:

$$yu^2 = -(2/A^2\overline{M}_n) + (2/A)u \qquad (2)$$

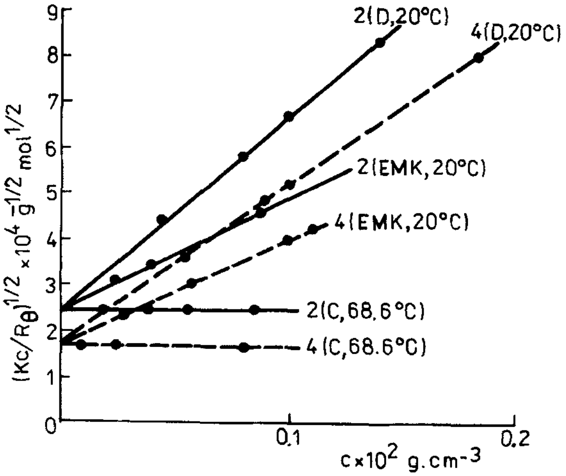

FIG. 3. Reciprocal square root of reduced scattering intensity at zero scattering angle as a function of concentration for Samples 2 (—) and 4 (- -) (see Table 2) in D, EMK, and C.

where

$$u = (4\pi/\lambda)^2 \sin^2 (\theta/2)$$

$$A = \langle S_0{}^2 \rangle / M$$

Figure 3 presents the dependence of the reciprocal square root of the reduced scattering intensity at zero scattering angle as a function of concentration for Samples 2 and 4 (Table 2) studied in three different solvents. A_2 appears to be zero in cyclohexanol at 68.6°C (theta solvent)

Figure 4 gives the yu^2 vs u variation for the same samples in cyclohexanol at 68.6°C, according to Eq. (2). The data were used to determine the values given in Table 2.

Weight-average molecular weights, second virial coefficients, and gyration radii were obtained by processing the experimental data yielded by measurements of diffusion angles lower than 45° (Table 3).

The following equations have been established for the dependence of the mean-square radius of gyration on $\overline{M}_w$:

$$\langle S^2 \rangle = 2.00 \times 10^{-18} \overline{M}_w^{\,1.174} \qquad \text{(D, 20°C)} \qquad (3)$$

$$\langle S^2 \rangle = 7.944 \times 10^{-18} \overline{M}_w \qquad \text{(C, 68.6°C)} \qquad (4)$$

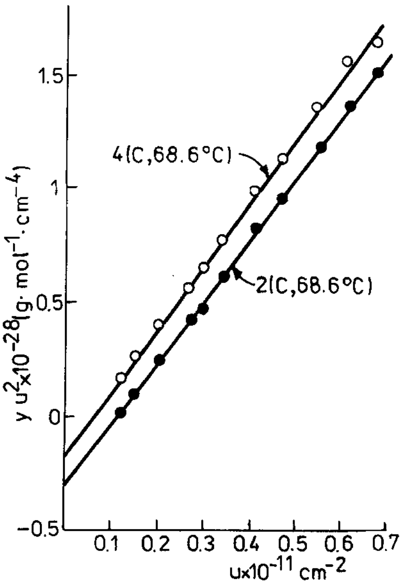

FIG. 4. Plots of yu^2 vs u for Samples 2 and 4 (see Table 2) in C, at 68.6°C.

TABLE 3. Second Virial Coefficient A_2 and Root-Mean-Square Radius of Gyration $\langle S^2 \rangle^{1/2}$ (unperturbed: $\langle S_0^2 \rangle^{1/2}$) for MMA-S 50:50 mol/mol Copolymers at 20°C in 1,4-Dioxane and at 68.6°C in Cyclohexanol

	1,4-Dioxane		Cyclohexanol,
Sample	A_2, 10^{-4} $cm^3 \cdot mol \cdot g^{-2}$	$\langle S^2 \rangle^{1/2}$, 10^{-5} cm	$\langle S_0^2 \rangle^{1/2}$, 10^{-5} cm
1	2.291	1.414	0.719
2	1.910	2.498	1.187
3	1.863	2.638	1.244
4	1.701	3.831	1.680
5	1.556	4.872	2.068
6	1.481	5.357	2.244

These equations are in agreement with the theory of polymer solutions with the exponent equal to unity for the theta solvent. The dependence of the second virial coefficients A_2 on $\overline{M}_w$ led to

$$A_2 = 5.408 \times 10^{-3}\overline{M}_w^{\,-0.20} \qquad (\text{D}, 20^\circ\text{C}) \tag{5}$$

The slope is negative, as expected for flexible linear polymers. For very large values of the excluded parameter Z and according to the available theories, -0.20 is considered to be a limit value.

The dependence of A_2 on $\overline{M}_w$ is modified with increasing molecular weight, while the dependence of $\langle S^2 \rangle$ on $\overline{M}_w$ remains unchanged (Eqs. 3-5). In these conditions, the values resulting from experimental data for $\Psi(Z)$ can differ from those expected according to theories concerned with dilute solutions of linear flexible polymers.

The following combinations permit a discussion of $\Psi(Z)$ calculated on the basis of different theoretical and approximate expressions established for α_s and $\Psi(Z)$ [21]:

Combination Y (the Kurata-Yamakawa theory of Ψ with the Yamakawa-Tanaka theory of α_s):

$$\alpha_s^{\,2} = 0.541 + 0.459(1 + 6.04Z)^{0.46} \tag{6}$$

$$\Psi(Z) = 0.547[1 - (1 + 3.903\overline{Z})^{-0.4683}] \tag{7}$$

Combination F,o (the original Flory-Krigbaum-Orofino theory of Ψ and the original Flory theory of α_s):

$$\alpha_s^{\,5} - \alpha_s^{\,3} = 2.60Z \tag{8}$$

$$\Psi(Z) = (2.30)^{-1} \ln(1 + 2.30\overline{Z}) \tag{9}$$

Combination F,m (the modified Flory-Krigbaum-Orofino theory of Ψ and the modified Flory theory of α_s):

$$\alpha_s^{\,5} - \alpha_s^{\,3} = 1.276Z \tag{10}$$

$$\Psi(Z) = (5.73)^{-1} \ln(1 + 5.73\overline{Z}) \tag{11}$$

The values obtained from Eqs. (6)-(11) for $\Psi(Z)$ in dioxane are represented as a function of $\alpha_s^{\,3}$ in Fig. 5.

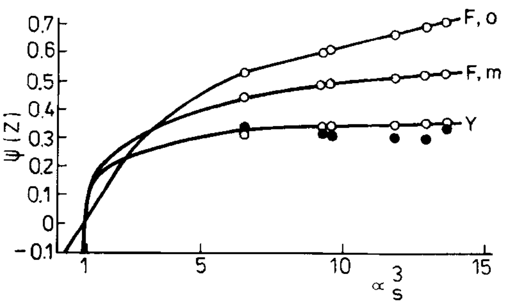

FIG. 5. Plots of $\Psi(Z)$ vs α_s^3 for MMA-S 50:50 random copolymers in D at 20°C (●). The curves represent the theoretical values (○) determined according to Eqs. (6)-(11).

One can see reasonable agreement between the curve calculated according to Eqs. (6) and (7) and the data points calculated from Eq. (1), taking into account that some sources of systematic errors can appear, e.g., the polydispersity of polymer samples or the calculation of α_s from the ratio of gyration radii evaluated at quite different temperatures

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are both in fair agreement with the experimental data, while differences seem to appear when α_s^3 has greater values.

To verify the theoretical predictions showing that α_s^5 for linear flexible polymers is asymptotically proportional to Z, the dependence of these parameters was studied according to the relation established by Domb and Barrett [22]:

$$\alpha_s^2 = (1.53 \pm 0.01)Z^{2/5} \tag{12}$$

Figure 6 shows the obtained results, and it also includes literature data based on the theories of Flory [23] and Yamakawa-Tanaka [24].

Therefore, in the ultrahigh molecular weight region, expansion of a macromolecular coil increases with excluded volume, as predicted by theory. It seems that the second virial coefficient, defined as a measure of all interactions existing in the system, is responsible for the appearance of some anomalies between experimental and theoretical data.

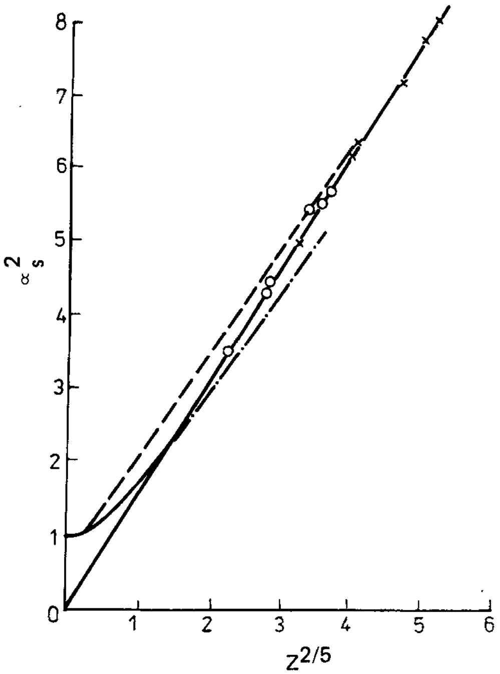

FIG. 6. Plots of α_s^2 vs $Z^{2/5}$ for MMA-S copolymers in D (○) and EMK (×) (present data); (- -) original Flory equation [23]; (—) Domb-Barrett equation [22]; (-·) Yamakawa-Tanaka equation [24].

CONCLUSION

The plasma-induced copolymerization technique proves to be an interesting tool for the synthesis of ultrahigh molecular weight copolymers (pleistomers). The reaction mechanism involves living radicals. Both the molecular weight and the compositional heterogeneity of the resulting copolymers are small.

Many difficulties arise during the characterization of pleistomers, but extension of the molecular weight scale is an important experimental test for different theoretical equations. At the same time, new approaches should be developed.

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