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Interpretation of long-chain structure from dilute solution properties of ultrahigh molecular weight polymers

Maria Bercea[1], Silvia Ioan[1], Bogdan C. Simionescu[2,*], and Cristofor I. Simionescu[1]

[1]"P. Poni" Institute of Macromolecular Chemistry, RO-6600 Jassy, Romania
[2]Department of Macromolecules, Polytechnic Institute of Jassy, RO-6600 Jassy, Romania

Summary

Systematic studies on solution properties of ultrahigh molecular weight polymers showed the existence of some special features as compared to usual length polymers. The paper discusses the possible appearance of branched structures in the polymerization process, structures able to influence the mentioned features. From experimental data on poly(methyl methacrylate), poly(butyl methacrylate) and polyacrylonitrile it appears that branching can be excluded, and the very high molecular weight domain considered may be responsible for the modifications observed in the molecular weight dependences on $\langle S^2 \rangle$, A_2 or $[\eta]$.

Introduction

During the last decade a lot of experimental work on solution properties of ultrahigh molecular weight polymers prepared by plasma-induced polymerization was published (1-9). These macromolecular compounds appeared to present some special properties as compared to usual length polymers, namely (a) low molecular weight and (for copolymers) compositional heterogeneity, (b) less visible and pronounced conformational changes as a function of temperature and solvent nature, (c) an increased rigidity of the macromolecular chains in dilute solution, as shown by the established relations between the radii of gyration, the second virial coefficients and/or the intrinsic viscosities and the molecular weight, and (d) for high values of the expansion factor ($\alpha_s^3 > 4$), from the theories permitting the discussion of the interpenetration function $\psi(Z)$, the experimental data are in good agreement with the Kurata - - Yamakawa theory (10) and with the new theory of Douglas and Freed (11). In this context, the possible errors appearing in studying the solution properties of ultrahigh molecular weight polymers by use of light scattering and viscometry were minimized through specific restrictions and calculation techniques (1, 12).

The present paper considers the possibility of the formation of branched structures during the plasma-induced polymerization of methyl methacrylate, butyl methacrylate and acrylonitrile as a possible explanation of the differences observed between the experimental data and literature data reported for usual length, linear polymers with the same chemical structure.

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[*] To whom offprint requests should be sent

Experimental

The synthesis of poly(methyl methacrylate) (PMMA), poly(butyl methacrylate) (PBuMA) and polyacrylonitrile (PAN) samples, the preparation of the solutions, as well as the light scattering and viscometric measurements of the studied polymers were previously described (1-9, 13, 14).

Results and Discussion

The possible formation of branched structures during the plasma-induced polymerization process was analysed based on a comparison of the experimental data with literature data obtained for linear polymers. The following results were considered:

For PMMA:

- experimental data:

$$\langle S_0^2\rangle = 7.806\times10^{-18}\bar{M}_w \quad (\mathrm{cm}^2) \qquad (1)$$

(CCl_4, 27°C - theta condition, light scattering, $\bar{M}_w = 7.5\times10^6 - 18.7\times10^6$) (4)

- literature data:

$$\langle S_0^2\rangle = 6.410\times10^{-18}\bar{M} \quad (\mathrm{cm}^2) \qquad (2)$$

(butyl chloride, 35.4°C - theta condition) (15)

$$\langle S_0^2\rangle = 6.820\times10^{-18}\bar{M} \quad (\mathrm{cm}^2) \qquad (3)$$

(various solvents, 25°C) (15)

$$\langle S_0^2\rangle = 7.110\times10^{-18}\bar{M} \quad (\mathrm{cm}^2) \qquad (4)$$

(benzene, toluene, 21°C) (15)

For PBuMA:

- experimental data:

$$\langle S_{0z}^2\rangle = 9.550\times10^{-18}\bar{M}_w \quad (\mathrm{cm}^2) \qquad (5)$$

$$\langle S_{0w}^2\rangle = 8.510\times10^{-18}\bar{M}_w \quad (\mathrm{cm}^2) \qquad (6)$$

$$\langle S_0^2\rangle = 7.240\times10^{-18}\bar{M}_w \quad (\mathrm{cm}^2) \qquad (7)$$

(DMF, 23.6°C - theta condition, light scattering, $\bar{M}_w = 11.90\times10^6 - 47.32\times10^6$) (3)

Eq. (7) was determined according to Debye's theory on the interference function for a Gaussian chain (2).

$$\langle S_0^2\rangle = 7.730\times10^{-18}\bar{M}_w \quad (\mathrm{cm}^2) \qquad (8)$$

(benzene, dioxane, cyclohexanone, methyl ethyl ketone (MEK), 25°C, by use of the method of Lenka et al. (16)), see Ref. (5).

- literature data:

$$\langle S_0^2\rangle = 5.889\times10^{-18}\bar{M}_w \quad (\mathrm{cm}^2) \qquad (9)$$

(DMF, 23.6°C - theta condition, light scattering) (17)

- experimental data:

$$[\eta] = 0.613\times10^{-4}\bar{M}_w^{0.7258} \quad (\mathrm{dl.g}^{-1}) \qquad (10)$$

(MEK, 25°C, $\bar{M}_w = 9.59\times10^6 - 21.63\times10^6$) (7)

- literature data:

$$[\eta] = 0.970\times10^{-4}\bar{M}_w^{0.680} \quad (\mathrm{dl.g}^{-1}) \qquad (11)$$

(MEK, 25°C, $\bar{M}_w = 11\times10^4 - 67\times10^5$) (15)

For PAN:

- experimental data:

$$<S_z^2> = 0.863\times10^{-18}\bar{M}_w^{1.26} \quad (\mathrm{cm}^2) \qquad (12)$$

$$<S_w^2> = 0.638\times10^{-18}\bar{M}_w^{1.26} \quad (\mathrm{cm}^2) \qquad (13)$$

(DMF, 20^{0}C, light scattering, $\bar{M}_w = 1.041\times10^6 - 3.078\times10^6$), see Refs. (13) and (14).

- literature data:

$$<S_z^2> = 1.613\times10^{-18}\bar{M}_w^{1.24} \quad (\mathrm{cm}^2) \qquad (14)$$

(DMF, 20^{0}C, light scattering, $\bar{M}_w = 1\times10^5 - 2\times10^6$) (18)

- experimental data:

$$[\eta] = 0.536\times10^{-4}\bar{M}_w^{0.839} \quad (\mathrm{dl.g^{-1}}) \qquad (15)$$

(DMF, 20^{0}C, $\bar{M}_w = 1.041\times10^6 - 3.078\times10^6$) (13, 14)

- literature data:

$$[\eta] = 4.660\times10^{-4}\bar{M}_w^{0.710} \quad (\mathrm{dl.g^{-1}}) \qquad (16)$$

(DMF, 20^{0}C, $\bar{M}_w = 1\times10^5 - 2\times10^6$) (18)

- experimental data:

$$A_2 = 9.44\times10^{-3}\bar{M}_w^{0.219} \qquad (17)$$

(DMF, 20^{0}C, $\bar{M}_w = 1.041\times10^6 - 3.078\times10^6$) (13, 14)

- literature data:

$$A_2 = 4.94\times10^{-2}\bar{M}_w^{0.27} \qquad (18)$$

(DMF, 20^{0}C, $\bar{M}_w = 1\times10^5 - 2\times10^6$) (18)

The overall of long chain branching parameters include so called branching degree defined for branched polymers as the ratio of a given polymer property of branched and linear macromolecules at the same molecular weight. Thus, the commonly used branching degrees are defined as:

$$g_\eta^3 = [\eta]_{br}/[\eta]_{lin} \qquad (19)$$

and

$$g_s^2 = <S^2>_{br}/<S^2>_{lin} \qquad (20)$$

The two branching degrees g_η^3 and g_s^2 are related by

$$g_\eta^3 = (g_s^2)^b \qquad (21)$$

where the branching exponent b depends above all on the type of branching, and it varies from 0.5 to 1.5 (19). The branching degrees g_η^3 and g_s^2 are equal to unity for linear polymers and are lower than unity for branched polymers.

As a rule, several methods have to be applied for determination of overall branching parameters, and the results have to be usually confirmed by one or more other methods and/or by theoretical assumptions.

Table 1 presents the results concerning branching for the samples under study - PMMA, PBuMA and PAN. The data were obtained according to eqs. (1) - (18).

It appears from Table 1 that the existence of branches can be excluded for ultrahigh molecular weight PMMA and PBuMA samples, obtained by plasma-induced polymerization, but remains under discussion for PAN samples. However, in the latest case, the observed behaviour may be due to the fact that the characteristics calculated from the literature may be inadequate for the molecular weight range discussed in the present paper and/or to the polydispersities of the samples.

Table 1. Theoretical predictions and experimental results for PMMA, PBuMA and PAN samples

Polymer	Parameter a)	Theor. prediction b)	Exptl. result	Eqs. used	Coincidence of exptl. result with theor. pred.
PMMA	g_s^2	<1	1.218	(1)-(2)	-
			1.145	(1)-(3)	-
			1.098	(1)-(4)	-
PBuMA	g_s^2	<1	1.622	(5)-(9)	-
			1.445	(6)-(9)	-
			1.229	(7)-(9)	-
			1.313	(8)-(9)	-
	g_η^3	<1	1.371	(10)-(11)	-
	g_η/g_s	>1	0.872	(10,11)-(5,9)	-
			0.924	(10,11)-(6,9)	-
			1.001	(10,11)-(7,9)	-
			0.969	(10,11)-(8,9)	-
	a_{MH-I}/a_{MH-II} c)	<1	1.067	(10)-(11)	-
PAN	g_s^2	<1	1.093	(12)-(14)	-
			0.811	(13)-(14)	+
	g_η^3	<1	0.733	(15)-(16)	+
	g_η/g_s	>1	0.862	(15,16)-(12,14)	-
			1.002	(15,16)-(13,14)	-
	a_{MH-I}/a_{MH-II} c)	<1	1.183	(15)-(16)	-
	A_{2-I}/A_{2-II}	<1	0.362	(17)-(18)	+
	$(A_2M/[\eta]_I)/(A_2M/[\eta]_{II})$	<1	0.491	(17,15)-(18,16)	+

a) values I - polymers obtained by plasma-induced polymerization, values II - literature data for linear polymers
b) for plasma-induced polymerization branched polymers
c) a represents the exponent in the Mark - Houwink relation

At the same time, the experimental results obtained according to Table 1, generally differing from unity, could be due to a specific behaviour of these ultrahigh molecular weight polymer samples which, as previously discussed (1-9), differ from the classical behaviour as described by the existing theories.

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