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Plasma-Induced Polymerization

9. "Living" Radical Copolymerization of Methyl Methacrylate and Styrene

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SUMMARY

Experimental and theoretical data proving the existence of long-lived ("living") poly(methyl methacrylate-co-styrene) 50:50 random macroradicals are presented.

INTRODUCTION

In some previously published papers, plasma-induced polymerizations and copolymerizations were reported (SIMIONESCU et al., 1980a, b; 1981a, b). The polymerization mechanism was shown to be a radical one, and some specific features of this new approach to polymer synthesis were underlined. In all cases, prolonged post-polymerization periods were observed, indicating considerable lifetime for propagating radicals, and these observations led to the ideea of the existence of "living" macroradicals in such systems. Their formation in both homogeneous and heterogeneous media was experimentally proved and theoretically explained, and their use as macromolecular initiators in polymerization processes was exemplified (SIMIONESCU et al., 1981c).

The plasma-induced polymerization of methyl methacrylate was investigated in detail by JOHNSON et al. (1981), and its copolymerization with styrene, by the same technique, was reported (SIMIONESCU et al., 1980a). The mentioned studies showed that homopolymerization yields ultrahigh molecular weight poly(methyl methacrylate) (e.g., in excess of 10^7), and that copolymerization leads to copolymers with compositions and configurations very close to those obtained by classical radical initiation ($r_{MMA} = 0.41 \pm 0.01$, $r_S = 0.57 \pm 0.01$).

The present paper is concerned with "living" radical copolymerization of methyl methacrylate and styrene, presenting both experimental and theoretical data on the long-lived macroradicals acting as propagating species.

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EXPERIMENTAL AND RESULTS

The general technique of plasma-induced polymerization was previously described.

The monomers were purified and dried by the usual methods. The initial mixture of the monomers (85 ml, 77.265 g styrene, and 85 ml, 79.560 g methyl methacrylate), calculated to yield 50:50 composition copolymers, was introduced in a long reaction tube, equipped with six lateral ampoules, connected to the main tube through necks for sealing. The system was evacuated to 10^{-3} - 10^{-4} Torr and then a 60 seconds electrical discharge was operated at 15 mm from the sample. Immediately following the discharge, the mixture was omogenized, and then equal amounts of solution (28.33 ml) were introduced in each of the lateral ampoules which were detached by sealing of and kept in dark, at room temperature. The samples were opened after different periods of time, diluted with benzene and precipitated in methanol.

^{1}H-NMR spectra confirmed that 50:50 random copolymers were yielded.

Weight average molecular weights ($\overline{M}_w$) were obtained by light scattering measurements, performed on a PCL Peaker apparatus, in methyl ethyl ketone (MEK).

Number average molecular weights ($\overline{M}_n$) were calculated from light scattering data obtained in cyclohexanol (θ solvent, 68.6°C, according to FROELICH and BENOIT (1966)), using the Debye theory, considering the particle scattering function of a molecular-weight polydisperse sample of linear flexible polymer in the unperturbed state (MIYAKI et al., 1978). Elaboration of these data will be subject of a further communication.

Weight and number average molecular weights, obtained in MEK and cyclohexanol (C), are given in Table 1.

TABLE 1
$\overline{M}_w$ and $\overline{M}_n$ data of the copolymers

Sample	$\overline{M}_w$(MEK) $\times 10^{-7}$	$\overline{M}_w$(C) $\times 10^{-7}$	$\overline{M}_n$(C) $\times 10^{-7}$	$\overline{M}_w/\overline{M}_n$(C)
1	0.7323			
2	1.7974	1.8321	1.1268	1.626
3	2.0175			
4	3.9544	3.7250	2.4890	1.497
5	5.7668			
6	6.5966			

The evolution of copolymer yield and molecular weight is presented in Figure 1.

According to these experimental data, the copolymeri-

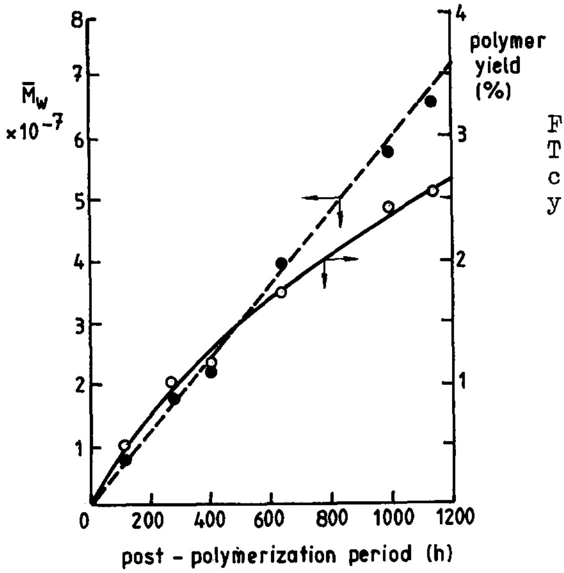

Figure 1.
Time dependence of copolymer $\overline{M}_w$ and yield

zation process continues for very long periods of time after the initiation took place; the data were used to estimate the evolution of the concentration of macroradicals (per ml), $N_{R\cdot}$, given by

$$N_{R\cdot} = g\cdot N_A/\overline{M}_n\cdot v$$

where g is the amount of copolymer formed in the ampoule, in grams, N_A is the Avogadro number, $\overline{M}_n$ is the average number molecular weight of the sample, and v is the volume of the sample contained in each ampoule (28.33 ml).

The data were processed for three different cases - $\overline{M}_w/\overline{M}_n = 1.0$ (hypothetical monodisperse polymer; actual "monodisperse" "living" polymers have the polydispersity index 1.01 - 1.05), $\overline{M}_w/\overline{M}_n = 1.5$ (addition polymers, termination by coupling, low conversion), and $\overline{M}_w/\overline{M}_n = 2.0$ (addition polymers, termination by disproportionation, low conversion). It should be mentioned that it was considered that, from sample 1 to sample 6, all macroradicals remain active, and that their length is very close to the average length.

The obtained results are presented in Table 2. Considering the real polydispersity index, calculated based on data obtained in cyclohexanol, the concentration of macroradicals was found to be $5.217\cdot 10^{14}$ (sample 2) and $3.631\cdot 10^{14}$ (sample 4).

The data presented are only approximative values; it should be mentioned, however, that in a classical bulk polymerization (copolymerization) system, considering the initiator concentration as being 1% based on the

TABLE 2
Evolution of the concentration of macroradicals

Sample	Concentration of macroradicals		
	$\bar{M}_w/\bar{M}_n=1.0$ $N_R.(x10^{-14})$	$\bar{M}_w/\bar{M}_n=1.5$ $N_R.(x10^{-14})$	$\bar{M}_w/\bar{M}_n=2.0$ $N_R.(x10^{-14})$
1	3.978	5.968	7.957
2	3.208	4.813	6.417
3	3.167	4.750	6.334
4	2.426	3.640	4.853
5	2.322	3.483	4.644
6	2.186	3.279	4.372

weight of monomer (monomers), the concentration of the formed radicals is between 10^{19} and 10^{21}, so 10^5 - 10^7 times more important.

DISCUSSION

The present results demonstrate the existence of "living" macroradicals in methyl methacrylate - styrene plasma-induced bulk copolymerization. Their formation is normal, considering that

i - the initiation efficiency is small, so that a small number of radicals become growing macroradicals by adding monomer molecules;

ii - the transfer constants to both monomers have very small values (about 10^{-4}; for instance, the transfer constant to styrene, at 0°C, is 0, and increases only slightly up to room temperature (BRANDRUP and IMMERGUT, 1975);

iii - the transfer constants to the formed copolymer are also very small (about 10^{-4}) at room temperature and, even if it appears, leads to branched macroradicals, able to continue the molecular weight growth; for so important chain lengths, however, intramolecular chain transfer has to be considered, but its presence doesn't limit the magnitude of the molecular weight;

iv - in order for the chemical recombination to take place, macroradicals must come into contact with one another, but, in a very viscous milieu, correspondingly to the increase of macroradical length, the mobility and the probability of recombination decrease; the same observations have to be considered for disproportionation reactions.

Our results are not the only ones existeng on "living" macroradicals; in a recently published review on the kinetics of polymerization processes, BERLIN et al. (1981) considered "living" radical polymerization and copolymerization and the formation, under certain conditions, of "living" radical polymerization centers.

The concentration of the macroradicals decreases only very slightly in time (Table 2) so that, while the molecular weight of the copolymer grows, the number of chains remains almost constant.

Certainly, the post-polymerization rate has to decrease in time - but for very important post-polymerization periods -, as a rezult of either the annihilation (by chemical transformation) of the macroradicals, or of their "immurement" in the formed polymer (physical deactivation).

"Living" radical processes open up new and interesting possibilities of synthesis, previously characteristic of ionic "living" systems, e.g., the production of block copolymers and the obtaining of polymers (copolymers) with a narrow molecular weight distribution. Experimental results in the last direction will be published in the future.

REFERENCES

BERLIN,A.AL., VOLFSON,S.A. and ENIKOLOPIAN,N.S.: Adv. Pol.Sci. 38, 89 (1981)

BRANDRUP,J. and IMMERGUT,E.H. (Editors): Polymer Handbook, 2nd edition, New York: John Wiley & Sons 1975

FROELICH,D. and BENOIT,H.: Makromol.Chem. 92, 224 (1966)

JOHNSON,D.R., OSADA,Y., BELL,A.T. and SHEN,M.: Macromolecules 14, 118 (1981)

MIYAKI,Y., EINAGA,Y. and FUJITA,H.: Macromolecules 11, 1180 (1978)

SIMIONESCU,B.C., NATANSOHN,A. and SIMIONESCU,C.I.: Polymer Bull. 2, 809 (1980a)

SIMIONESCU,B.C., LEANCA,M., ANANIESCU,C. and SIMIONESCU,C.I.: Polymer Bull. 3, 437 (1980b)

SIMIONESCU,B.C., LEANCA,M., IOAN,S. and SIMIONESCU,C.I. Polymer Bull. 4, 415 (1981a)

SIMIONESCU,B.C., NATANSOHN,A., LEANCA,M., ANANIESCU,A. and SIMIONESCU,C.I.: Polymer Bull. 4, 569 (1981b)

SIMIONESCU,C.I., SIMIONESCU,B.C., LEANCA,M. and ANANIESCU,C.: Polymer Bull. 5, 61 (1981c)

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