

Plasma-induced polymerizations and copolymerizations*

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The paper deals with plasma-induced homo- and copolymerizations, insisting on specific features of this new approach to polymer synthesis and on the properties of the obtained polymers. The formation of "living" macroradicals and their use as macromolecular initiators in polymerization processes is exemplified.

Работа посвящена плазматически индуцированным гомо- и сополимеризации, причем упор делается на специфические черты этого нового подхода к синтезу полимеров и новых свойств получаемых полимеров. Продемонстрировано образование «живучих» макрорадикалов и их использование в качестве макромолекулярных инициаторов процессов полимеризации.

Plasma-induced polymerization (copolymerization) is a new method of polymer synthesis in macromolecular plasma chemistry [1, 2]. In this particular case, the initiation reaction takes place in the gas phase and can be easily controlled, the relative molecular mass and polydispersity of the resulting polymers are directly related to the reaction conditions, and the activity of the propagating species appears to be unusually high and very stable in time, even at room temperature. The polymerization reactions initiated in this manner yield ultrahigh relative molecular mass compounds and occur at room temperature.

These reasons strongly justify the interest in studying plasma-induced polymerization (copolymerization) reactions, in order to observe and underline some features and advantages of the method.

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Experimental

The general experimental procedure was previously described [3, 4]. The monomers were purified with great care before use, introduced in polymerization ampoules, frozen in liquid nitrogen after degassing, evacuated to 10^{-1} — 10^{-2} Pa and sealed. Electrical discharges were then operated between two electrodes situated on each ampoule at 4.0 and 6.5 cm from the sample (monomer or comonomer mixtures) and coupled to a high frequency discharge generator (frequency 2.5 MHz, power 100 W); a third electrode, uncoupled to the generator, was situated at 2.0 cm from the sample, in order to limit the discharge and to impede it to touch the frozen sample. The discharge were operated during 30—180 s. The samples were kept in the dark, at room temperature, and opened after different periods of time to separate the polymer.

The relative molecular masses of the polymers were determined either by light scattering measurements (M_{LS}), or by viscosity measurements (M_{LV}). Number-average relative molecular masses were calculated from light scattering data obtained in θ solvents, using the Debye theory, considering the particle scattering function of a relative molecular mass polydisperse sample of linear flexible polymer in the unperturbed state [5, 6].

Light scattering studies were performed on a P.C.L. Peaker apparatus, at 25 °C, at 436 nm, using measurements ranging from 40° to 140°.

Copolymer structure was determined by ^1H -n.m.r. spectroscopy on a Jeol C-60 spectrometer. The data were processed according to the Kelen—Tüdös method.

Results and discussion

1. Plasma-induced homopolymerizations and copolymerizations

The results on plasma-induced bulk and solution homopolymerization of some vinylic monomers are presented in Table 1. The data show that ultrahigh or high relative molecular mass polymers are yielded, even if in some cases only small conversions are reached. The bulk polymerization of acrylic acid and solution polymerization of acrylamide prove that yields can be considerably improved by modifying the reaction conditions.

Data on bulk copolymerization of four different monomeric systems are given in Table 2. Microstructural studies of part of these copolymers showed that their configurations are very close to those of similar compounds obtained by classical radical copolymerization [3, 7, 8], and, at the same time, the reactivity ratio values are quite identical. From these observations, one can conclude that a radical mechanism of polymerization has to be taken into account in such processes; this mechanism was also confirmed by inhibition experiments with hydroquinone.

Table 1
Plasma-induced bulk and solution homopolymerizations

Monomer and polymerization conditions	Polymer	
	Yield/%	M_{LS} or M_{LV}
Bulk homopolymerization		
— styrene, 180 s discharge, 1080 h (post-polymerization period)	18	$M_{LS} = 3.9 \times 10^7$
— acrylic acid, 60 s, 3 h	100	$M_{LS} = 2.2 \times 10^6$
— methacrylic acid, 60 s, 240 h	1.2	$M_{LV} = 1.4 \times 10^7$
— methyl methacrylate, 60 s, 120 h	2.7	$M_{LS} = 1.6 \times 10^7$
Solution homopolymerization		
— <i>N</i> -vinyl carbazole/benzene, 60 s, 720 h	3.8	$M_{LV} = 1.8 \times 10^4$
— styrene/benzene, 60 s, 240 h	0.3	$M_{LV} = 4.9 \times 10^4$
— acrylamide/water, 60 s, 240 h	7.9	$M_{LS} = 1.4 \times 10^7$

Table 2
Plasma-induced bulk copolymerizations

Copolymerization system (M_1 — M_2)	r_1	r_2	σ
Methyl methacrylate—styrene	0.41	0.57	0.48
Methyl methacrylate— α -methyl styrene	0.42	0.22	0.21
Acrylonitrile— α -methyl styrene	0.03	0.14	
Methacrylonitrile—styrene	0.21	0.34	1.00

σ — probability of alternating coisotactic addition, determined from $^1\text{H-n.m.r.}$ spectra.

2. Compositional and relative molecular mass heterogeneity of plasma-obtained polymers

Data on heterogeneity of chain composition of methacrylonitrile—styrene copolymers obtained by plasma-induced technique are presented in Table 3. More data concerning this aspect as well as the used method are given in [9] and for methyl methacrylate—styrene copolymers in [10]. For all compositions, the average apparent relative molecular masses (M_{ap}) are slightly dependent on the determination solvent. The compositional heterogeneity results, given by Q/Q_{max} ratio, are collected in Table 4, as well as true mass average relative molecular mass data.

Table 3
Average apparent relative molecular masses of methacrylonitrile—
—styrene copolymers

Sample	Copolymer composition/%		$M_{sp} \cdot 10^{-5}$			
	MAN	S	MEK	D	DMF	C
1	70.33	29.67	10.000	9.981	9.987	10.050
2	54.75	45.25	15.063	15.392	15.482	15.883
3	47.65	52.35	14.985	15.334	15.428	15.818
4	40.83	59.17	16.282	16.509	16.579	16.837
5	32.43	67.57	11.792	12.022	12.080	12.292

MEK — methyl ethyl ketone; D — dioxan; DMF — dimethylformamide; C — chloroform.

Table 4
Compositional heterogeneity data and true mass average relative molecular masses of methacrylonitrile—styrene copolymers

Sample	Q/Q_{max}^*	$\bar{M}_w \cdot 10^{-5}$
1	0.381	10.060
2	0.413	14.894
3	0.452	14.795
4	0.403	16.173
5	0.392	11.645

* Q/Q_{max} may be defined as a quantitative measure of the compositional heterogeneity and its maximum value is 1; for more details see Ref. [9].

Results on 50:50 methyl methacrylate—styrene random copolymers of different relative molecular masses are summarized in Table 5, together with some relative molecular mass polydispersity data.

Plasma-induced bulk homopolymerization of methyl methacrylate was studied in detail, at different reaction conditions (Table 6), in order to obtain information on the kinetics of the process. Preliminary results prove that this new method of polymer synthesis may be used to obtain uniform relative molecular mass (“mono-disperse”) polymers.

All these data show that the copolymers exhibit a small compositional and relative molecular mass polydispersity and the homopolymers have a low polydispersity. One has to underline also that the reaction conditions are directly related to the relative molecular mass characteristics of the resulting compounds.

product separates as a solid crystalline compound as it forms. After purification from chloroform and methanol at low temperature the product melts at 133 °C with decomposition.

Experimental

4,4'-Azo-bis(4-cyanovaleryl) chloride

To a chilled slurry of 10 g (0.0357 mol) of 4,4'-azo-bis(4-cyanovaleric) acid in 100 ml of dry benzene in a 500 ml three-neck flask equipped with mechanical stirrer, thermometer, and condenser with drying tube, phosphorus pentachloride (20 g; 0.0959 mol) was added during 25 min. Stirring was continued for a few minutes at ice temperature, and the reaction mixture was then allowed to stay overnight at room temperature, when all but slight residue had dissolved. The solution was then filtered and phosphorus oxide trichloride and benzene were evaporated in vacuum under low pressure at 30—40 °C. The resulting yellow solid was dissolved in methylene chloride and reprecipitated out with cold heptane.

4,4'-Azo-bis(4-cyanovaleryl)-4-nitrobenzoyl diperoxide

Pyridine (1.78 ml; 22.1 mmol) is added in portions to a chloroformic solution of 4-nitroperbenzoic acid (4.04 g; 22.1 mmol) cooled at -3 °C, maintaining the temperature below 0 °C. The reaction mixture becomes clear, acid chloride (3.5 g; 11.1 mmol) solved in anhydrous chloroform (25 ml) is added dropwise from a funnel provided with CaCl₂ tube, during 30—40 min maintaining the temperature within the 0—2 °C range. The reaction mixture is then stirred at 0—5 °C for 5 h, allowed to stay overnight at this temperature and filtered. 5.1 g of white-yellow precipitate are thus obtained from which pyridinium chloride and excess of 4-nitroperbenzoic acid are removed by washing with 15 ml of cold CH₃OH (-20 °C). 4.3 g of white-yellow solid product are thus obtained ($\eta = 31.93\%$). The filtrate was washed with cold water (50 ml), 10 % aqueous Na₂CO₃, again with cold water (50 ml) and then dried on Na₂SO₄ and filtered. The resulting chloroformic solution is concentrated under vacuum at 20—25 °C. A crystalline yellow solid product is thus obtained.

Results and discussion

In the i.r. spectrum (Fig. 1) the doublet characteristic of the CO group in diacylperoxides is to be found, at 1760 cm⁻¹ (CO—CH₂ more intense) and 1800 cm⁻¹ (CO—Ph—NO₂). Other elements in agreement with the above structure are: $\nu_s(\text{NO}_2)$ (1340 cm⁻¹), $\nu_{as}(\text{NO}_2)$ (1530 cm⁻¹), $\nu(\text{C}\equiv\text{N})$ (2240 cm⁻¹).

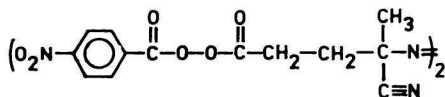
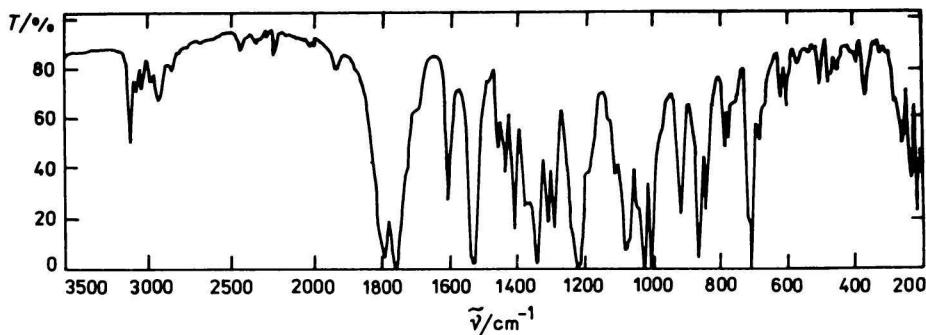


Fig. 1. Infrared spectrum of 4,4'-azo-bis(4-cyanovaleryl)-4-nitrobenzoyl diperoxide.

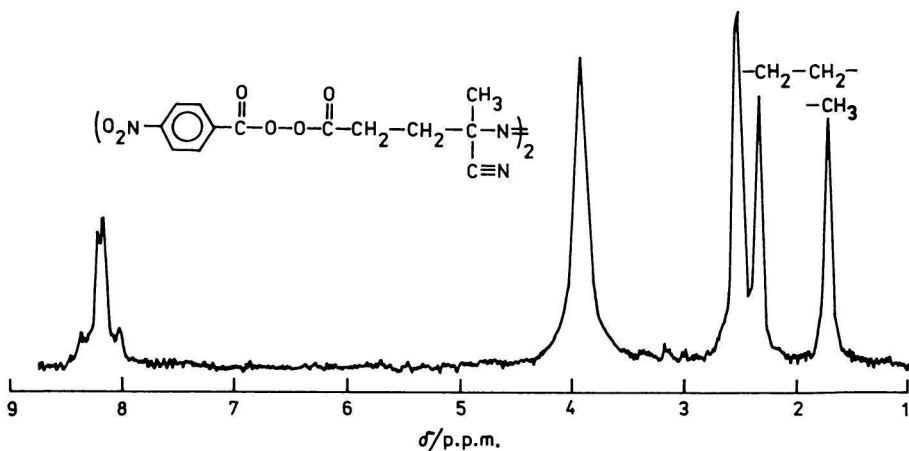


Fig. 2. ¹H-N.m.r. spectrum of 4,4'-azo-bis(4-cyanovaleryl)-4-nitrobenzoyl diperoxide.

The ¹H-n.m.r. spectrum (Fig. 2) was recorded at 60 MHz with an INM-C-Gohl apparatus by using DMSO-d₆ as a solvent. The proton signals are identified at the chemical shifts (δ values, p.p.m.): 1.7 (CH₃ singlet), 2.3 (CH₂—CH₂, singlet, protons magnetically equivalent), 8.2 (aromatic protons, signal of the AA'BB' type centred at the indicated value, characteristic of the *p*-substituted benzene ring) and correspond to the number of existing protons.