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Plasma-Induced Polymerization

3. Bulk and Solution Homopolymerization of Some Vinylic Monomers

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SUMMARY

Preliminary results on plasma-induced bulk homopolymerization of styrene, acrylic acid, methacrylic acid, ethyl acrylate and on plasma-induced solution homopolymerization of N-vinyl carbazole, styrene and acrylamide are presented. Experimental data suggest that a radical mechanism of polymerization has to be considered to explain this new approach to polymer synthesis.

INTRODUCTION

In two previously published papers the plasma-induced bulk copolymerization of methyl methacrylate and styrene (SIMIONESCU et al., 1980a) and of alpha-methyl styrene with methyl methacrylate and with acrylonitrile (SIMIONESCU et al., 1980b) was reported. The high molecular weight polymers obtained were shown to have compositions and configurations very close to those obtained by radical mechanisms. At the same time, in the first mentioned paper we refered to the potential interest of this new approach to polymer synthesis for the obtention of homopolymers, copolymers and block copolymers.

The present paper deals with some preliminary data on bulk and solution homopolymerization of certain vinylic monomers performed by plasma-induction. Our attention was focused on bulk polymerization of styrene, acrylic acid, methacrylic acid, ethyl acrylate, and on solution polymerization of N-vinyl carbazole, styrene and acrylamide.

EXPERIMENTAL

Liquid monomers were twice distilled at reduced pressure, under nitrogen, dried on CaH_2, redistilled and used immediately after. Acrylamide and N-vinyl carbazole were twice recrystallized before use. Unless specified, the monomers (or their solutions) were in-

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troduced in Pyrex ampoules, frozen in liquid nitrogen after degassing, evacuated to 10^{-1}-10^{-2} Torr and sealed. The ampoules were submited to electrical discharges operated between two electrodes situated at 1.0 and 2.0 cm from the sample, coupled to a high frequency discharge generator (frequency - 2.5 MHz, power - 100 W). The discharge was operated during 60 seconds. The samples were kept at room temperature, in dark, and opened after different periods of time.
Control experiments were carried out simultaneously. In these experiments the discharges were omitted and, under these conditions, homopolymerizations did not take place or take place in unsignificant amounts and led to small molecular weight polymers.
The molecular weights of the obtained polymers were determined either by viscosity measurements (M_{LV}), using the limiting viscosity number - molecular weight relationship $[\eta] = KM^a$, or by light scattering (M_{LS}).

RESULTS AND DISCUSSION

1. Plasma-induced bulk homopolymerization of styrene.

The discharge was operated during 540 seconds and the sample was opened after 45 days, diluted with benzene and precipitated in methanol. The yield was found to be 0.91% and the M_{LS} $3.87 \cdot 10^7$ (control experiment: M_{LS} $1.20 \cdot 10^5$).
It has to be mentioned that the yield of the polymerization can be considerably increased by changing the conditions of the reaction (e.g. the vacuum in the ampoule before the discharge, the plasma duration, the post-polymerization time). All the experiments performed with styrene led to very high molecular weight polymers (M_{LS} $2.00 \cdot 10^6$ - $4.00 \cdot 10^7$); yields up to 18% were obtained.

2. Plasma-induced bulk homopolymerization of acrylic acid.

The ampoule containing the monomer was evacuated at 10^{-4}-10^{-5} Torr. The sample was opened three hours after the discharge, due to the very rapid appearance of a white polymer in the reaction milieu, disolved in methanol and precipitated in benzene. The conversion reached about 100%; the M_{LS} was determined to be $2.21 \cdot 10^6$. The polymer was partially soluble in dioxane and soluble in water.

3. Plasma-induced bulk homopolymerization of methacrylic acid.

The sample was opened 10 days after the discharge, diluted with methanol and precipitated in diethyl ether. The yield was 0.47%; considering $K=242 \cdot 10^{-3}$ ml/g and $a=0.51$ (methanol solution, 26°C, according to WIEDER-

HORN and BROWN, 1952), the M_{LV} was found to be $1.35 \cdot 10^7$.

4. Plasma-induced bulk homopolymerization of ethyl acrylate.

The sample was kept in dark during 9 days, precipitated in n-heptane, disolved in benzene and reprecipitated. The yield was 0.80% and the M_{LV} $9.32 \cdot 10^6$ ($K=27.7 \cdot 10^{-3}$ ml/g, a=0.67, benzene solution, 30°C, according to SUMITOMO and YACHIHAMA, 1955).

5. Plasma-induced solution homopolymerization of N-vinyl carbazole.

6.0 g (0.031 mole) N-vinyl carbazole in 50 ml benzene were taken in the reaction; the sample was opened after 30 days and precipitated in methanol. The yield was 3.78% and the M_{LV} $1.81 \cdot 10^4$ ($K=3.05 \cdot 10^{-2}$ ml/g, a=0.58, benzene solution, 25°C, according to SITARAMAIAH and JACOBS, 1970).

6. Plasma-induced solution homopolymerization of styrene.

20 ml (0.174 mole) styrene in 40 ml benzene were taken in the reaction; the sample was kept in dark during 10 days. The polymer was precipitated in methanol. The yield was 0.30% and the M_{LV} $4.95 \cdot 10^4$ ($K=11.3 \cdot 10^{-3}$ ml/g, a=0.73, benzene solution, 25°C, according to BAWN et al., 1950).

7. Plasma-induced solution homopolymerization of acrylamide.

6.0 g (0.084 mole) acrylamide in 25 ml H_2O were taken in the reaction; the sample was opened after 10 days. The polymer was diluted with water and precipitated in methanol. The yield was 7.95 and the M_{LS} $1.37 \cdot 10^7$.

The above presented results do not emphasize all our experiments concerning the plasma-induced homopolymerization. In some cases we failed in obtaining more than traces of polymers (e.g. bulk homopolymerization of vinyl acetate, acrylonitrile, n-butyl acrylate, and solution homopolymerization of N-vinyl carbazole). As concerns the polymerization mechanism, a radical one has to be taken into account. The following observations led to this conclusion:

(i) - the bulk copolymerization of methyl methacrylate with styrene as well as the bulk copolymerization of alpha-methyl styrene with methyl methacrylate or with acrylonitrile showed monomer - copolymer composition relations identical to those for classical free radical copolymerization; the coisotactic alternating addition probability for the first two systems also indicate a radical mechanism of copolymerization;

(ii) - the polymerization doesn't occur in presence

of radical polymerization inhibitors, but the presence of water doesn't impede the propagation;
(iii) - the presence of oxygen in the reaction milieu decreases the polymer yield and increases the polymer molecular weight. Detailed data on this effect will be published in the near future.

CONCLUSIONS

Plasma-induced bulk and solution homopolymerization leads to ultrahigh or high molecular weight polymers. Even if small amounts of polymers are obtained in such reactions, the results on bulk homopolymerization of acrylic acid and styrene, as well as on solution homopolymerization of acrylamide show that yields can be considerably improved. It has to be mentioned that not all the monomers tested polymerized by plasma-induction.

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