Polymer Bulletin 26, 409–416 (1991)

Polymer Bulletin

Plasma polymerization and copolymerization of styrene and methylmethacrylate

I. Plasma initiated polymerization studies

Bilge Özden (Orhan) and Güneri Akovalı*

Department of Chemistry and Macromolecular Research Division, (Tumka) Middle East Technical University, TR-06531 Ankara, Turkey

Synopsis

Plasma initiated polymerization and copolymerization is applied to two model compounds, styrene and methylmethacrylate, in a series of experiments. For this polymerization tubes with break seals in the middle having two different compartments are used. For samples without and with break seals-the latter is broken right after discharge-a random copolymer rich product; while for the others with break seals broken after certain times, a block copolymer is obtained, as traced out by NMR and IR studies.

Introduction

Plasma polymerization is drawing considerable interest in recent years especially after having several of it's highly promising applications. Numerous papers are already published on plasma polymerization of different conventional and unconventional monomers; by using "plasma initiated" and "plasma state" polymerizations, respectively. Our existing knowledge on it's mechanism is still far from complete, and a better understanding is needed.

To gain more information on plasma polymerization, two model compounds (styrene (S) and methyl methacrylate (MMA) are tested in liquid (plasma initiated) and in gas phase (plasma state) polymerizations in a series of experiments. First part of this study which is presented here deals with some results obtained from plasma initiated polymerization and copolymerization of these model compounds.

Plasma initiated polymerization of (S) in bulk is reported to yield to "trace amounts of" insoluble film in one study (1) which notes "no post-polymerization"; and to a high molecular weight polymer with considerably high yields via "living styrene macroradicals" in an another study (2,3); where, being quite contradictory to the first, "considerable post-polymerization after plasma initiation" is also noted.

---

*To whom offprint requests should be sent

Plasma initiated polymerization of (MMA) is found to yield to ultrahigh (Ca, 3x10^7) molecular weight polymers with quite high yields (1;4-6). Reaction was shown to be free radicalic (7-9) and the main precursor was claimed to be a "biradical which is assumed to be produced in vapor" (9). There are also studies to specify the main active specie (10-12).

Plasma initiated bulk copolymerization of (S) and (MMA) are investigated first by Osada (1) where the inhibiting effect of (S) monomer on copolymerization reaction is noted. Increasing (S)concentrations in the feed up to 40% decrease yields steadily; and at this value, "discoloration and insoluble film formation" were again noted. Reaction was shown to proceed with a free radical mechanism and a random copolymer was obtained. In the study of Simionescu et. al., (13), free radical mechanism for the reaction was again approved and the copolymer obtained had very high molecular weights. In an another study of the same group, the concentration of living macroradicals in copolymerization medium were calculated as 10^5-10^7 times higher than in a classical bulk copolymerization system (14). There were no indication of separation of homopolymers from copolymeric products in these publications (13,14).

Experimental

The monomers used, (S) and (MMA) were products of BASF and Aldrich Chem. Co., respectively. Both were purified first by removal of inhibitor by standard procedure followed by distillation. During plasma studies, an r.f. generator operating at 13.56 MHz coupled to a matching network and a wattmeter was used. The Osada-Bell and Shen's procedure (1) was applied during copolymerization studies, except the pyrex polymerization tubes (10 cm. in length and 2 cm. in dia.) had a break-seal in the middle; hence it had two compartments for two different monomers used. By this method, we were able to initiate plasma either in "both" or in "any" of the compartments on wish, simply by adjusting the location of outer electrodes. Hence control of the plasma-initiation and post-polymerization reactions were possible for any period of time before or after mixing the monomers. For this, first; equal volume of monomers were vacuum distilled into separate compartments,degassed sealed and kept frozen at liquid nitrogen temperature. The ampoule then inserted between a pair of parallel plate electrodes connected capacitively to (r.f.) and discharge power was put on until droplets of liquid appeared, after which glow was generated in the tube and continued for about 3 min. or more. The ampoule was then left to stand in a constant temperature bath (30°C, unless specified otherwise) for 168 hrs. of total post-polymerization time; meanwhile seal-break was broken for certain samples at certain times. After completion of post-polymerization, the ampoule was broken, its contents were precipitated with methanol; filtered and dried in vacuum oven.

For all samples except the ones with trace amounts of products, "selective precipitation" was applied (15) to separate homo-and co-polymers. For this, known amounts of product was dissolved in benzene to form a (2%) solution which was diluted with equal volume of acetone afterwards. Equal volume of petroleum ether (PE) was added slowly over it with stirring, during which PMMA precipitates. After filtration, the supernatant was recovered by evaporating the solvent, solid was dissolved in equal volumes of benzene and chlorobenzene and than methanol was added slowly until no further precipitation (of PS). The products were analyzed by use of Bruker (200 M Hz) ^{1}H.N.M.R. and I.R. spectrometers.

As pointed out by Bovey (16), Overberger (17) and others (18-19); random and block copolymers of (MMA/S) couple have common peaks between 7-6.5 ppm (phenyl protons). In the random copolymers with high (S) feeds, the ortho ring protons appear as a smaller peak or even as a shoulder at higher field than that of meta and para; whereas at lower (S) feed ratios, only a single peak is seen (16). For random copolymers, the peaks for methoxyl protons (MMA) are seen in 3.6-2.1 ppm region and CH_2 (MMA) and $CHCH_2$ protons (S) appear in 1.9-1.5 ppm. region. At highest field, 1.2-0.5 ppm. peaks are due to the α-methyl groups (MMA). Whereas for block copolymers, there is a 3.6 ppm. singlet due to methoxy (MMA) and a doublet α-methyl protons between 1.2-0.5 ppm. (17). Overberger also showed that the N.M.R. spectra of anionically prepared block copolymer is exactly the same with that of a mixture of two homopolymers of (MMA) and (S) and their block copolymer can not be clearly distinguishable from each other easily, except by a slight difference in (C-O-C) stretching bands at 1280-1150 cm^{-1}; whereas for a random copolymer, a broad band appears in the same region withouth effecting the characteristic bands of 1740 cm^{-1} (C=O; MMA) and 690 cm^{-1} (S).

Composition of products were obtained by I.R. by use of a precalibrated curve (prepared by using the characteristic band intensity ratios of 1740 cm^{-1} (C=O) to 690 cm^{-1} (monosubstituted phenyl in a series of blends) which were also checked by N.M.R.

Results and Discussion

Two different set of results were obtained from two different procedures used, depending on:

a) whether discharge was applied to one compartment or to both, and,

b) lenghth of time waited to break the seal after the discharge.

Results are presented in (Table I. and II). Results of first group of experiments with discharges applied to both compartments yielded to trace amounts of products in general as also was noted by Osada et. al (13). Although magnitude of yields seem to be unaffected by the parameters like discharge periods, temperature and even by the time to break the seal after discharges (Table I), both compositions and the nature of products were apparently influenced considerably by these parameters. First three experiments for samples withouth and with break seals-the latter is broken right after

TABLE I. Results of experiments with discharges applied to both compartments.

Exp.No.	Discharge Period (Min)	Time to Break The Seal After Discharge	%MMA in the Product (Moles)	%Conversion	Notes
1	3	-Right after discharge-	30	Trace	A random copolymer rich product
2	3	-Right after discharge-	29	Trace	A random copolymer rich product. Post Polym.temp: 90°C
3	3	-No break seal used-	36	Trace	A random copolymer rich product
4	3	52	58	Trace	A block copolymer rich product (or a mixture of homo-polymers)
5	3	120	54	Trace	"
6	10	24	42	Trace	"
7	3	24	79 (before extr.) 5 (Methanol ppd.)	13.6	A block copolymer

Discharge conditions: Frequency 13.56 mHz., Power 20 Watts.
Volume of (S) and (MMA) were equal to each other.
Total Post Polymerization Time: 168 hours.
Post Polymerization Temperature: (before and after breaking seal): 30°C (unless specified otherwise)

TABLE II. Results of experiments with discharges applied to one compartment only.

Exp.No.	Discharge Period (Min)	Time to Break The Seal After Discharge(hrs)	% MMA in the Product (moles)	% Conversion	Notes
8	3 (to MMA only)	-Right after discharge-	20	Trace	A random copolymer rich product
9	3 (to S only)	-Right after discharge-	15	2.3	"
	3 (to S only)	24	65 (PE.ppt.) 5 (methanol ppd)	5.8	A block copolymer
10	3 (to MMA only)		54 (Before extr.) 60(PE.ppt)	6.0	"

Discharge conditions : Frepuency 13.56 mHz., 20 Watts.
Volume of (S) and (MMA) were equal to each other.
Total Post Polymerization Time: 168 hours.
Post Polymerization Temperature: (before and after breaking the seal): 30°C

discharge-yielded to "random copolymer rich" products with similar composition (Fig. 1 and 2a); bearing random copolymer characteristics.

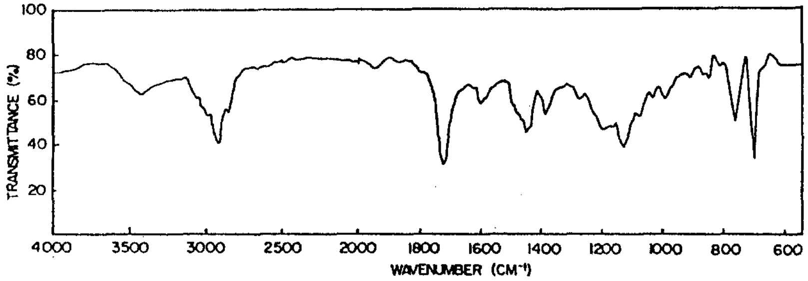

Figure 1. IR Spectrum of random copolymer (exp. 3) (film from $CHCl_3$)

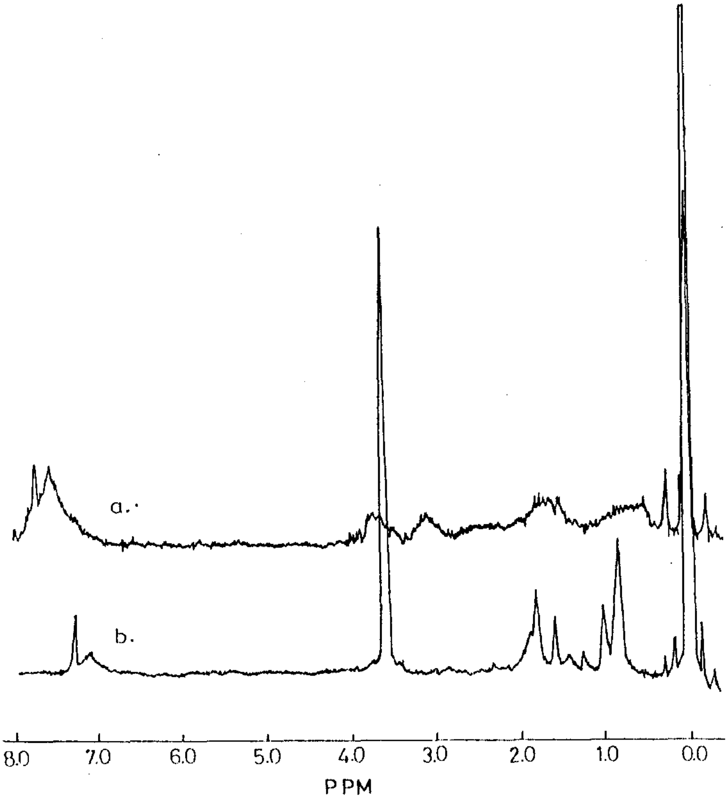

Figure 2a.NMR spectrum of random copolymer (exp. 3)
b.NMR spectrum of a block copolymer (exp.7)

Increase of temperature did not change (MMA) content in the random copolymer. On the other hand, it is interesting to see that; all the samples with break seals broken after certain times did not yield to random but most probably to "block copolymers", (Fig.2b and 3). As the amount of products obtained in experiments 1 to 6 were too low, no selective precipitation was applicable to separate homopolymers from the system. In addition, although it would be possible to differentiate a random and a block copolymer (of S and MMA) spectrometrically; this method was mentioned as not suitable to trace out block copolymers of this couple from the mixture of their homopolymers. Hence, products of 1 to 3 rd experiments were labelled as "random copolymer-rich" and both "block copolymer-rich or mixture of homopolymer" alternatives were used for the rest, in (Table I.).

Figure.3 presents IR of (sample 7) and NMR of same sample is given in (Figure.2b); which clearly show block-copolymer structure. As traced out from selective precipitation steps, during copolymerization, homopolymers and even one-component rich copolymers were unaviodably produced.

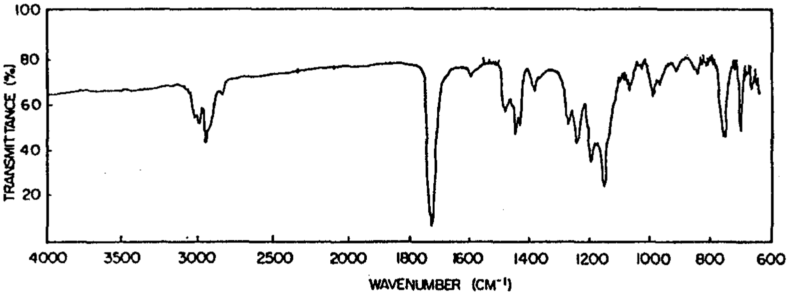

Figure 3.IR Spectrum of Block Copolymer (exp. 7) (film from $CHCl_3$)

The result obtained in second group of experiments where discharge was applied to one compartment only yielded to similar results and they are presented in(Table.II). Hence it is interesting to conclude that, if S and MMA monomers were isolated from each other for certain periods of time after their activation by plasma; a block copolymer is obtained being irrespective of either both or one of the monomers were activated.

ACKNOWLEDGEMENTS The authors wish to thank to TUBİTAK (Turkish National and Scientific Research Council) through TUMKA Unit and to METU-University Research Fund. AFP-87-01-03-09

References

1. Osada Y, Bell A.T and Shen- M. "Plasma Polymerization" A.T.Bell and M.Shen, editors. A.C.S. Symposium Series. (1979) 108.253

2. Simionescu B.C., leance M., Ananiescu C., Simionescu C.I. -Polymer Bull.(1980) 3. 437 .

3. Simionescu C.I., Sinionescu B., Leance M., Anamiescu C. -Polymer Bull.(1981) 5. 61

4. Kashinwagi Y., Einaga Y., Fujita H.-Polymer J.(1980) 12.4.271

5. Demirel G., Akovalı G.- J.Poly.Sci. Polym.Chem (1985) 23.2377

6. Osada Y., Takase Y.- J.Poly.Sci.Lett. (1983) 21.643

7. Akovalı G., Demirel G., Özkan S.- J.Macromol.Sci.Chem. (1983) A20.8.887

8. Akovalı G., Demirel G.- METU J. of Pure and Appl.Sci. (1983) 16.2/3.201

9. Johnson D.R., Osada Y., Bell A.T. and Shen M. J.Poly.Sci.Poly.Lett. (1979) 16. 669 and ibid- Macromol.(1981) 14.118

10. Kuzuya M., Kamiga K., Kawaguchi T., Okuda I.- Polymer Lett. (1983) 21.509

11. Paul C.W., Bell A.T. and Soong D.S.-Macromol. (1985)18.2312. and ibid. (1985) 18.2318.

12. Paul C.W., Bell A.T. and Soong D.S. Macromol. (1986) 19.1431

13. Simionescu C.I., Natansoku N. and Siminoescu B. -Polymer Bulletin. (1980) 2. 809 .

14. Simionescu C. I., Popa Ion and Simionescu B. -Polymer Bulletin. (1982) 6. 415.

15. Urwin J.R. and Stearne J.M.-Makromol.Chem. (1964) 78. 194

16. Bovey, F.A., J.Polym. Sci., (1962), 62, 197

17. Overberger, C.6., Yamamoto, N., Polymer Letters., (1965) 3, 569

18. Ito, K., Yamashita, Y., Polymer Letters, (1965) 3,625

19. Ito, K., Yamashita, Y., Polymer Letters, (1965) 3, 631

Accepted June 15, 1991 C