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Plasma-induced Polymerization

5. Bulk Copolymerization of Methacrylonitrile with Styrene

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SUMMARY

High molecular weight methacrylonitrile (M_1) - styrene (M_2) copolymers were obtained by plasma-induced bulk copolymerization. The reactivity ratios, determined by Kelen - Tüdös method, were shown to be r_1=0.21 and r_2=0.34 and indicate a radical mechanism of polymerization. Some microstructural aspects of the obtained copolymers are presented.

INTRODUCTION

In some 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 acrylonitrile (SIMIONESCU et al., 1980b) was reported. The reactivity ratio values, as well as the value of the configurational parameter σ (for the first two systems) indicated the radical nature of the plasma-induced process.

The present paper deals with the plasma-induced bulk copolymerization of methacrylonitrile (MAN, M_1) and styrene (S, M_2), studying several microstructural aspects of the obtained polymers.

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EXPERIMENTAL

The monomers were twice distilled at reduced pressure under nitrogen, dried on CaH_2, redistilled and used immediately after. The comonomer mixtures were introduced in Pyrex ampoules, frozen in liquid nitrogen after degassing, evacuated to 10^{-3}-10^{-4} Torr and sealed. Electrical discharges were then operated between two electrodes situated at 2.5 and 3.5 cm from the comonomers sample; the electrodes were coupled to a high-frequency discharge generator (frequency - 2.5 MHz, power - 100 W). The discharge was generated during 300 seconds. The samples were kept in dark, at 22.5° C, during 24 days, opened, diluted with benzene and precipitated in methanol.

^{1}H-NMR spectra were registered in $CDCl_3$ solutions at 60° C and in pyridine solutions at 100° C, on a JEOL-C-60 spectrometer. Copolymer composition was determined from the ratio aromatic / aliphatic integrals in the spectra registered in $CDCl_3$, while microstructural information was obtained from the spectra registered in pyridine. The α-CH_3 resonances were decomposed in three main parts using a curve resolving program on a JEC-6 computer.

RESULTS AND DISCUSSION

Copolymerization data are given in Table 1.

The copolymerization diagram is presented in figure 1.

Data processing according to the Kelen - Tüdős equation (figure 2) gives the results r_1=0.21 and r_2=0.34. The points lie on a straight line, indicating that the terminal model of copolymerization could characterize the system.

For radical copolymerization of MAN and S, the reactivity ratios given in Table 2 were obtained.

TABLE 1

Copolymerization data

Sample	Initial mixture $x=[M_1]/[M_2]$	Conversion (%)	Copolymer composition $y=d[M_1]/d[M_2]$	Inherent viscosity*
1	7.00	5.35	2.37	1.414
2	3.00	3.42	1.46	1.938
3	1.67	7.12	1.21	2.054
4	1.00	7.06	0.91	2.106
5	0.60	6.15	0.69	2.306
6	0.33	10.83	0.51	1.884
7	0.14	12.63	0.48	1.689

* - measured at a concentration of 0.5 g/dl, in $CHCl_3$, at 24° C

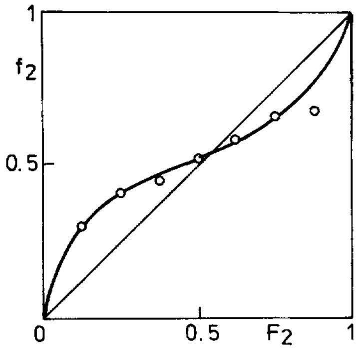

Fig. 1. Copolymerization diagram.

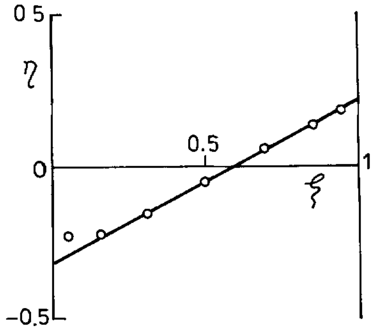

Fig. 2. The Kelen - Tüdös plot.

The CH_2 and α-CH_3 resonances are given in figure 3. α-methyl signal splitting was previously interpreted by MURANO et al. (1969) and by PATNAIK and GAYLORD (1971) in two different ways.

MURANO et al. supposed the main three parts of α-CH_3 signal (noted A, B and C in figure 3) to belong to 111 (A), 211+112 (B) and 212 (C) triad sequences. They compared the calculated triad fractions with the expe-

TABLE 2

MAN - S reactivity ratio values

Reactivity ratios		recalculated*		Copolymerization conditions		Reference
r_1	r_2	r_1	r_2	(solvent,	temp.)	
0.16	0.30	0.26	0.35	-	60	(a)
0.26	0.38	0.25	0.36	-	80	(b)
0.32	0.39	0.33	0.38	toluene	60	(c)
0.25	0.25			-	80	(d)
0.28	0.43			-	80	(e)
0.41	0.37			toluene	90	(c)
0.42	0.38			toluene	120	(c)
0.26	0.17			-	50	(f)

* - by the Kelen - Tüdős equations (GREENLEY, 1980)
(a) LEWIS et al., 1948; (b) CAMERON et al., 1959; (c) RUDIN and YULE, 1971; (d) FORDYCE et al., 1948; (e) BRANDRUP and IMMERGUT, 1975; (f) MURANO et al., 1969.

rimental A, B and C areas and obtained a fairly good concordance.

PATNAIK and GAYLORD studied the alternating MAN - S copolymer obtained by radical copolymerization. By analogy with other acrylic - vinyl aromatic copolymers, they assigned the α-CH_3 splitting to the aromatic screening effect of the styrene nuclei being on the same side of the main chain with the α-CH_3 group. The authors concluded that in these copolymers the coisotacticity tendency is very high (a meso 12 diad having the aromatic nucleus and the α-CH_3 group on the same side of the main chain).

The steric model for a 1_m2 diad, represented in figure 4, suggests that the α-CH_3 group should be very affected by the aromatic screening effect of a neighbouring styrene ring. Therefore, the PATNAIK and

GAYLORD interpretation seems to be more adequate.

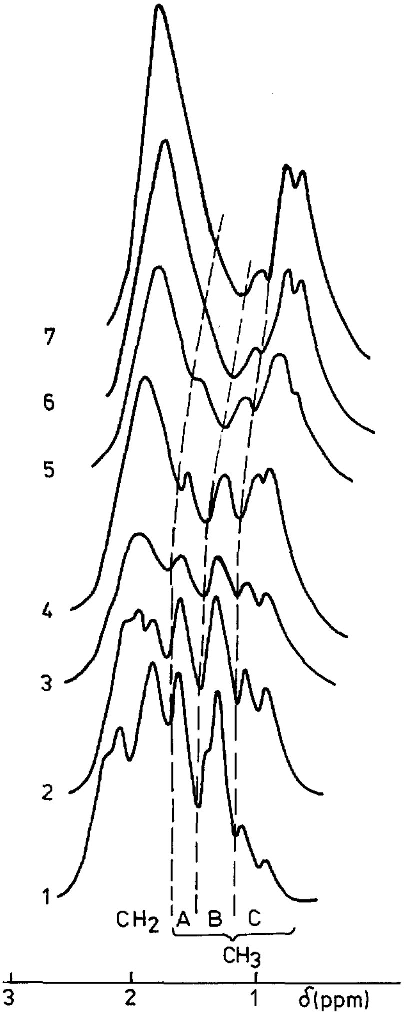

Fig. 3. Aliphatic resonance region of the ^{1}H-NMR spectra registered in pyridine at 100° C.

Moreover, the slight high-field shift of the A, B and C parts of the α-CH_3 signal when increasing styrene content in copolymers, could be a substitution effect, as observed in other analog systems (e.g., methyl methacrylate - styrene (SAN ROMAN et al., 1979) and methyl acrylate - phenylacetylene (SIMIONESCU et al., 1981)).

Consequently, we analysed the α-CH_3 signal splitting in terms of sequence distribution and configuration using the equations proposed by HARWOOD et al. (1969) for methyl methacrylate - styrene copolymers and applied by many authors on other acrylic - vinyl aromatic systems:

$$F_A = f_{111} + (1 - \sigma)f_{211} + (1 - \sigma)^2 f_{212}$$
$$F_B = \sigma f_{211} + 2\sigma(1 - \sigma)f_{212}$$
$$F_C = \sigma^2 f_{212}$$

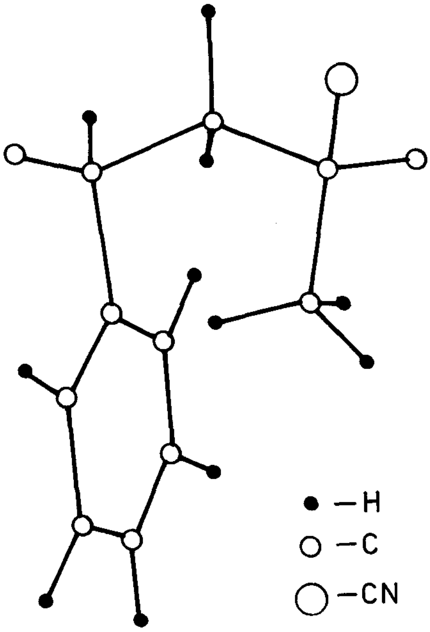

Fig. 4. Steric model of a coisotactic alternating diad.

Triad sequence fractions were calculated according to HARWOOD and RITCHEY (1964):

$$f_{111} = P_{11}^2$$
$$f_{211} = 2P_{11}P_{12}$$
$$f_{212} = P_{12}^2$$

where

P_{ij} is the probability of a j monomer addition at a i-ended macroradical, $F_{A,\ B,\ C}$ is the fraction of the A, B, C part of α-CH_3 signal and σ is the probability of a 1_m2 diad existence.

The ^1H-NMR spectrum of polymethacrylonitrile shows no α-CH_3 splitting due to different configurations. Such splitting was obtained only at 220 MHz in CD_3CN (SUZUKI et al., 1973); in fact, this was a fortunate situation, because in many similar cases the α-CH_3 signal is too complicated to be completely assigned.

Figure 5 presents the calculated triad fractions together with experimental $F_{A, B, C}$.

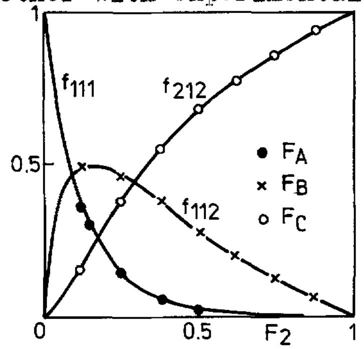

Fig. 5. Calculated (lines) and experimental (points) fractions of α-methyl resonance.

As it can be seen, $F_A = f_{111}$, $F_B = f_{211}$ and $F_C = f_{212}$ on all domain; therefore, σ must be 1.

The results are quite similar to those of MURANO et al., but the assignment is that of PATNAIK and GAYLORD. Further splitting, mainly of the C part of the signal, can be observed, but difficult to be assigned. The σ value of the system is rather high. A similar "stereoregularity" was found for methyl acrylate - 2-vinyl pyridine copolymers (NATANSOHN et al., 1979). Research on ^{13}C-NMR spectra of these copolymers will unambigously elucidate the sequence distribution and will clarify the configurational parameter value.

CONCLUSIONS

The relative reactivities of MAN and S at 22.5° C are 0.21 and 0.34; this proves again the radical nature of the plasma-induced process. ^{1}H-NMR spectra of these copolymers can be analysed in terms of sequence distribution and configuration. The configurational parameter indicates a high tendency of coisotacticity between phenyl and α-methyl groups.

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