

Free-Radical Copolymerization of 9-Vinylanthracene

D. KATZ, *Scientific Department, Israel Ministry of Defence, Tel-Aviv, and*
J. RELIS, *Bar-Ilan University, Ramat-Gan, Israel*

Synopsis

Free-radical copolymerization of methyl acrylate, ethyl acrylate, butyl acrylate, and methyl methacrylate with 9-vinylanthracene was studied, and the reactivity ratios r_1 and r_2 were calculated. In the light of earlier data on copolymerization of 9-vinylanthracene with styrene results show that the difference in polarity of the monomers participating in the copolymerization has an insignificant influence compared with that of the steric factors involved in the reaction.

INTRODUCTION

Free-radical polymerization of 9-vinylanthracene (9-VAn) and its copolymerization with styrene were reported earlier.^{1,2} In view of the good scintillation properties of 9-VAn,³ the interesting behavior of the monomer in polymerization processes,²⁻⁹ and the possibilities of using its copolymers as plastic scintillators² and organic semiconductors,¹⁰ the free-radical copolymerization with additional vinyl monomers was studied.

In the copolymerization process with styrene 9-VAn showed low reactivity, mainly attributed to the aplanarity of the 9-VAn molecule with steric hindrance of the exocyclic double bond by the bulky anthracene system.² As styrene and 9-VAn are of the same polarity, the present study was undertaken in order to ascertain whether copolymerization of 9-VAn would proceed more readily with monomers of opposite polarity. The monomers used were methyl acrylate (MAc) ethyl acrylate (EAc), butyl acrylate (BAc), and methyl methacrylate (MM).

EXPERIMENTAL

Preparation of 9-Vinylanthracene

The synthesis of 9-VAn, based on acetylation of anthracene in the 9 position, reduction of the acetylanthracene, and dehydration of the carbinol were described earlier.¹ Small modifications in the original acetylation procedure,¹¹ such as lowering of the temperature range from about 5-0° to about -10° to -5° and heating of the reaction mixture after addition of the AlCl_3 to +5° instead of +10° increased the efficiency of this step from 57-60 to 73%. The methyl acrylate, ethyl acrylate, and methyl methacrylate were obtained from British Drug Houses, Ltd., the

butyl acrylate from Rohm & Haas Company, and the di-*tert*-butyl peroxide from the Lucidol Division, Wallace & Tiernan Inc. After removal of the inhibitor with a 5% solution of NaOH the monomers were purified by additional distillation.

Copolymerization

Four series of experiments were conducted for the study of copolymerization of 9-VAn with each of the other monomers. In each series six test tubes containing 9-VAn, the other monomer, and the catalyst were sealed under reduced pressure in an atmosphere of dry N₂, the pressure at the moment of sealing being about 1 mm. Hg. The ratio of 9-VAn to the other monomer differed in each test tube, ranging from 10 to 60 mole-% 9-VAn. The amount of polymerization initiator (di-*tert*-butyl peroxide) used in the reaction was 3 mole-% per mole of monomer. The test tubes were kept in a thermostatic bath ($76 \pm 0.5^\circ$ for 9-VAn methyl acrylate and $78 \pm 0.5^\circ$ for the other systems) for different lengths of time. The polymerization process was interrupted before conversion reached 15% by opening the test tubes, dissolving their contents in methyl ethyl ketone, and precipitating the copolymers with *n*-heptane. Dissolution and precipitation of each polymer were repeated several times up to a constant weight of the dry polymer, after which the percentage of conversion was determined.

The composition of the copolymers was determined by measuring their specific extinction coefficients in chloroform solutions at 261/m μ . The equation used for calculation was

$$X = (E^* - E_B^*) / (E_A^* - E_B^*) \quad (1)$$

where X is the fraction of monomer A in the copolymer and E_A^* , E_B^* , and E^* are the specific extinction coefficients of homopolymer A, homopolymer B, and copolymer, respectively. This method, first used by Mechan in determining the composition of GR-S rubbers,¹² was also applied earlier in the study of the 9-VAn-styrene copolymerization.² The specific extinction coefficients measured at 261/m μ for the different polymers relating to

TABLE I
Copolymerization of Methyl Acrylate (M₁) with 9-Vinylnanthracene (M₂)
($76 \pm 0.5^\circ$, 3 mole-% di-*tert*-butyl peroxide)

No.	[M ₂] in init. monomer mixt., mole-%	Polymn. time, hr.	Convsn., %	E^* at 261 m μ	[m ₂] in copolymer, mole-%
1	10	166	1.84	7.65	3.43
2	20	210	1.21	16.10	7.61
3	30	234	1.13	23.30	11.59
4	40	258	1.02	29.60	15.45
5	50	261	0.96	38.80	21.65
6	60	330	1.13	46.51	27.52

this work were *p*-9-VAn 98.0, *p*-MAc 0.05, *p*-EAc 0.03, *p*-BAc 0.034, *p*-MM 0.08. Experimental results and calculated values of the 9-VAn content in the copolymers are listed in Tables I-IV.

TABLE II
Copolymerization of Ethyl Acrylate (M_1) with 9-Vinyanthracene (M_2)
($78 \pm 0.5^\circ$, 3 mole-% di-*tert*-butyl peroxide)

No.	[M_2] in init. monomer mixt., mole-%	Polymn. time, hr.	Convsn., %	E^* at 261 $m\mu$	[m_2] in copolymer, mole-%
1	10	193	1.65	6.10	3.10
2	20	330	0.95	12.41	6.63
3	30	333	0.78	20.04	11.16
4	40	380	0.75	27.68	16.26
5	50	476	1.24	36.91	22.92
6	60	499	1.27	45.10	29.54

TABLE III
Copolymerization of Butyl Acrylate (M_1) with 9-Vinyanthracene (M_2)
($78 \pm 0.5^\circ$, 3 mole-% di-*tert*-butyl peroxide)

No.	[M_2] in init. monomer mixt., mole-%	Polymn. time, hr.	Convsn., %	E^* at 261 $m\mu$	[m_2] in copolymer, mole-%
1	10	280	1.73	4.34	2.86
2	20	329	1.31	9.19	6.10
3	30	350	0.95	14.73	10.03
4	40	449	1.21	21.00	14.60
5	50	504	1.18	27.43	19.57
6	60	543	1.24	33.62	24.67

TABLE IV
Copolymerization of Methyl Methacrylate (M_1) with 9-Vinyanthracene (M_2)
($78 \pm 0.5^\circ$, 3 mole-% di-*tert*-butyl peroxide)

No.	[M_2] in init. monomer mixt., mole-%	Polymn. time, hr.	Convsn., %	E^* at 261 $m\mu$	[m_2] copolymer, mole-%
1	10	110	14.7	5.50	2.78
2	20	115	7.5	11.20	5.94
3	30	139	5.3	17.00	9.32
4	40	161	2.6	23.76	13.57
5	50	221	1.9	30.30	18.03
6	60	245	1.5	38.69	24.13

Data on the initial composition of the monomer mixtures (M_1 , M_2) and on the amount of monomers found in the copolymers (m_1 , m_2) were used for calculating the relative reactivities of 9-VAn and other monomers (r_1 , r_2). The copolymerization equation derived by Alfrey and Goldfinger¹³ and by Mayo and Lewis¹⁴ was applied in its graphic representation:

$$r_2 = [M_1]/[M_2]\{[m_1]/[m_2](1 + [M_1]/[M_2] r_1) - 1\} \quad (2)$$

For each copolymerization series a family of six straight lines (one for each experiment) was obtained in the r_1 - r_2 system of coordinates. Theoretically, each family of lines should have a single intersection point, but no concurrence could be obtained, owing to experimental errors, and mean values of r_1 and r_2 had to be calculated, allowing for different weights of the intersection points (nearly right-angled intersections being more important than acute-angled ones).

The equations used were:

$$r_2 = (m_1x_1 + m_2x_2 + \dots + m_nx_n)/\Sigma m_n \quad (3)$$

$$r_1 = (m_1y_1 + m_2y_2 + \dots + m_ny_n)/\Sigma m_n \quad (4)$$

where x_n and y_n are coordinates of the n th point of intersection, and m_n is the sine of the angle between the intersecting lines. This approach was already used by one of the authors in an earlier work.² The relative reactivities of the monomers obtained are listed in Table V.

TABLE V
Copolymerization of Methyl Acrylate, Ethyl Acrylate, Butyl Acrylate,
and Methyl Methacrylate (M_1) with 9-Vinylanthracene (M_2)

No.	M_1	M_2	r_1	r_2	Temp., °C.	di- tert- butyl per- oxide, mole- %
1	Methyl acrylate	9-Vinylanthracene	2.97	0.082	76 ± 0.5	3
2	Ethyl acrylate	"	3.43	0.274	78 ± 0.5	3
3	Butyl acrylate	"	3.76	0.163	78 ± 0.5	3
4	Methyl methacrylate	"	3.81	0.071	78 ± 0.5	3

CONCLUSIONS

In the light of earlier data on the copolymerization of styrene with 9-VAn² the present results show that the difference in polarity of the monomers participating in the copolymerization has an insignificant influence compared with that of the steric factors involved in the reaction.

References

1. E. D. Bergmann and D. Katz, *J. Chem. Soc.*, **1958**, 3226.
2. D. Katz, *J. Polymer Sci. A*, **1**, 1635 (1963).
3. A. Heller and D. Katz, *J. Chem. Phys.*, **35**, 1987 (1961).
4. H. Inoue, K. Noda, S. Takiuchi, and E. Imoto, *J. Chem. Soc., Japan, Ind. Ed.*, **65**, 128 (1962).
5. R. H. Michel, *J. Polymer Sci. A*, **2**, 2533 (1964).
6. A. Rembaum, H. Henry, and H. Waits, *Polymer Preprints*, **4**, 109 (1963).
7. R. H. Michel and W. P. Baker, *J. Polymer Sci. B*, **2**, 163 (1964).
8. A. Eisenberg and A. Rembaum, *J. Polymer Sci. B*, **2**, 157 (1964).
9. J. Moacanin and A. Rembaum, *J. Polymer Sci. B*, **2**, 979 (1964).
10. A. Rembaum, J. Moacanin, and H. Pohl, *Progr. Dielectrics*, **6** (1965).
11. C. Merritt and C. E. Brown, *Org. Syn.*, **30**, 1 (1950).
12. E. J. Mehan, *J. Polymer Sci.*, **1**, 175 (1946).
13. T. Alfrey, Jr. and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).
14. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

Received June 20, 1967

Revised December 11, 1967