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C. Bunel[a]; E. Marechal[b]
[a] Institut National Supérieur de Chimie Tndustrielle de Rouen, Mont Saint, Aignan, France [b] Laboratoire de Synthèse, Macromoléculaire Université, Paris, France

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Influence of Polymerization Temperature on Reactivity of 1- and 2-Vinyl Naphthalenes

CLAUDE BUNEL

Institut National Supérieur de Chimie Industrielle de Rouen
B.P. 08-76130 Mont Saint-Aignan, France

and

ERNEST MARECHAL

Laboratoire de Synthèse Macromoléculaire
Université P. & M. Curie
75005 Paris, France

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ABSTRACT

Reactivity ratios relative to the copolymerizations of 1-vinyl naphthalene and 2-vinyl naphthalene with styrene have been determined at different specific temperatures. In the case of the system 1-vinyl naphthalene-styrene, the Arrhenius plot exhibits a curve when the temperature is above -50°C. This is explained by the depropagation contribution. The value of the enthalpy of polymerization calculated by using the Lowry relation is in satisfactory agreement with that obtained from calorimetric determinations. From activation enthalpies and entropies it appears that the selection of the two monomers by the cation is entropically controlled for 2-vinyl naphthalene and enthalpically controlled for 1-vinyl naphthalene.

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INTRODUCTION

We have published several articles [1-6] relative to the cationic copolymerization of vinyl monomers with condensed rings in the molecule and, in particular, two articles [7, 8] relative, respectively, to the kinetics and to the transfers in the cationic polymerization of 1- and 2-vinyl naphthalenes. The present article reports the influence of the polymerization temperature on the reactivity of 1- and 2-vinyl naphthalenes.

EXPERIMENTAL

Monomers

Vinyl naphthalenes were synthesized by the methods of Berger [9] and Davis and Porter [10] by dehydration of 2-(1-naphtyl) and 2-(2-naphtyl) ethanols catalyzed by $KHSO_4$ in vacuo. 1-Vinyl naphthalene; yield 50%; n_D^{20} 1.6436; bp 80°C (0.5 mm). 2-Vinyl naphthalene: yield 50%; mp 66°C.

Styrene was freshly distillated before copolymerization.

Solvent

Methylene chloride was purified according to N'guyen Anh Hung [11].

Initiator

$TiCl_4$ was purified by distillation.

Copolymerization

These were carried out under nitrogen in a reactor equipped with a thermometer and a stirring system. When the monomer solution was at the specific temperature, the initiator solution was introduced with a pipette. After a few minutes the excess of initiator was destroyed by introduction of a mixture of methanol and methylene chloride.

RESULTS AND DISCUSSION

Reactivity ratios were determined by the Kelen and Tüdös method [12] which is derived from the classical Mayo-Lewis relation.

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TABLE 1. Copolymerization of 1-Vinyl Naphthalene (M_1) with Styrene (M_2). Dependence of Reactivity Ratios on Temperature. $[M] = 0.1$, $[TiCl_4] = 0.002$; Solvent CH_2Cl_2 ; T (°K) Is the Absolute Temperature of Polymerization

T (°K)	$10^3/T$	r_1	ln r_1	r_2	ln r_2
198	5.05	3.08	1.12	0.42	-0.87
201	4.98	2.90	1.06	0.60	-0.51
223	4.48	4.02	1.39	0.76	-0.27
223	4.48	3.95	1.37	0.65	-0.43
243	4.12	4.20	1.44	0.80	-0.22
248	4.03	4.07	1.40	0.82	-0.20
263	3.80	2.00	0.69	1.10	0.10
273	3.66	2.00	0.69	1.13	0.12

TABLE 2. Copolymerization of 2-Vinyl Naphthalene (M_1) with Styrene (M_2). Dependence of Reactivity Ratios on Temperature. $[M] = 0.1$; $[TiCl_4] = 0.006$; Solvent CH_2Cl_2 ; T (°K) Is the Absolute Temperature of Polymerization

T (°K)	$10^3/T$	r_1	ln r_1	r_2	ln r_2
198	5.05	2.68	0.99	1.08	0.08
223	4.48	3.59	1.28	1.12	0.11
243	4.12	4.10	1.41	1.25	0.22
273	3.66	4.10	1.41	1.75	0.56

Subscript 1 is relative to vinyl naphthalenes and Subscript 2 to styrene. The results relative to 1-vinyl and 2-vinyl naphthalenes are reported in Tables 1 and 2 and Figs. 1 and 2, respectively.

Discussion of the Results Relative to 1-Vinyl Naphthalene

The plot of ln r_1 against $10^3/T$ for 1-vinyl naphthalene (Fig. 1) is not a straight line. This is worth noting since straight lines have been obtained for most systems studied in cationic polymerization. Moreover, the experiments were performed three times by various workers and the results are perfectly reproducible. We have shown

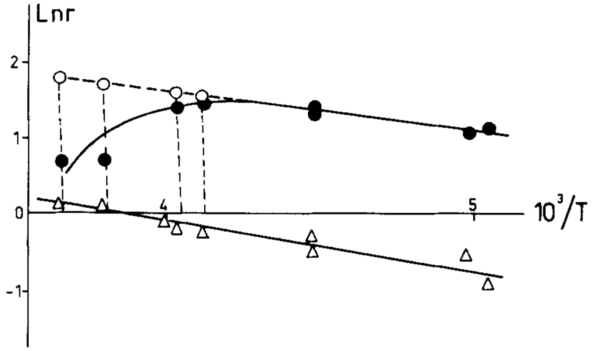

FIG. 1. The system 1-vinyl naphthalene-styrene. Dependence of r_1 and r_2 on the copolymerization temperature (T, °K). (●) ln r_1, (△) ln r_2, and (○) ln "r_1" (see text). (—) Experimental curves and (- -) extrapolation of the experimental straight line obtained between -50 and -72° C.

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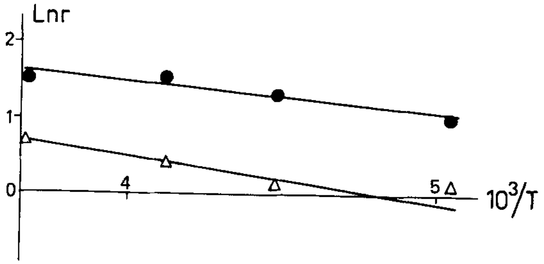

FIG. 2. The system 2-vinyl naphthalene-styrene. Dependence of r_1 and r_2 on the copolymerization temperature. (●) ln r_1 and (△) ln r_2.

that transfer cannot be responsible for this behavior. However, the study of the homopolymerization of 1-vinyl naphthalene has shown that the contribution of depropagation to the polymerization of this monomer increases with increasing temperature and is almost complete at room temperature. Lowry [13] has set out relations giving the composition of a copolymer when depropagation takes place; these relations have been obtained either by kinetic considerations or by probability calculations. Several cases which depend on the monomer which depropagates have been considered by Lowry. Let M_1 and M_2 be 1-vinyl naphthalene and styrene, respectively. We considered that depropagation takes place only between two M_1

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monomer units. This means that the only equilibria to be considered are

$$\sim\!\sim M_2M_1M_1^{\oplus} \rightleftharpoons \sim\!\sim M_2M_1^{\oplus} + M_1 \qquad k_{11},\ k_{11}' \qquad (1)$$

and

$$\sim\!\sim M_1M_1M_1^{\oplus} \rightleftharpoons \sim\!\sim M_1M_1^{\oplus} + M_1 \qquad k_{11},\ k_{11}' \qquad (2)$$

Let k_{11} and k_{11}' be the propagation and depropagation rate constants for both equilibria (1) and (2), and let α be $[(m_1)^*_{n+1}]/[(m_1)_n{}^*]$ where $[(m_1)_n{}^*]$ is the concentration of the active species: $\sim\!\sim M_2(M_1)_{n-1}M_1{}^{\oplus}$.

Lowry [13] has shown that:

$$Y = \frac{X\,[1/(1-\alpha)]}{r_2 + X} \qquad (3)$$

with $X = [M_1]/[M_2]$ and $Y = [m_1]/[m_2]$ where $[M_1]$, $[M_2]$, $[m_1]$, and $[m_2]$ are the monomer concentrations in the charge and in the copolymer. From (3) we established linear relation between r_1 and r_2:

$$r_2 = \frac{X^2}{Y}\left(1 - \frac{\alpha}{\rho[M_1]}\right) r_1 - \frac{X(Y-1)}{Y} \qquad (4)$$

and analyzed this relation as follows.

Relation (4) is similar to Mayo and Lewis:

$$R_2 = \frac{X^2}{Y} R_1 - \frac{X(Y-1)}{Y} \qquad (5)$$

Comparison of (3) and (4) leads to

$$R_2 = r_2 \qquad \text{and} \qquad R_1 = \left(1 - \frac{\alpha}{\rho[M_1]}\right) r_1 \qquad (6)$$

Let $1 - \alpha/\rho[M_1]$ be β; $\rho = k_{11}/k_{11}'$ is constant for a specific T:

$$\frac{\alpha}{[M_1]} = \frac{[(m_1)^*_{n+1}]}{[(m_1)_n^*][M_1]} = K$$

where k is the constant relative to

$$\sim\!\sim (M_1)_n^{\oplus} + M_1 \rightleftharpoons \sim\!\sim (M_1)_{n+1}^{\oplus} \tag{7}$$

and with $K < k_{11}/k_{11}'$ according to Sawada's [14] and Tobolsky's [15] studies on depropagation.

Thus it appears that β is constant and < 1, which explains why the Mayo-Lewis relation (5) (used to determine the reactivity ratios reported in Tables 1 and 2) gives a correct value for r_2 and an incorrect value for r_1 since $R_1 = \beta r_1$ is below r_1, which is the real value. This analysis is in complete agreement with Fig. 1.

By extrapolation of the straight line obtained between -72 and -50°C by plotting $\ln r_1$ vs $10^3/T$ (Fig. 1), we obtained the real values of r_1 ("r_1") for temperatures above -50°C.

It is possible to determine α and ρ from "r_1", r_2, $[M_1]$, $[M_2]$, X, and Y by using the following relations [13]:

$$\alpha = 1 - \frac{X}{Y(r_2 + X)} \tag{8}$$

and

$$\rho = \frac{\alpha - \alpha^2}{[M_1](1 - \alpha) - \dfrac{\alpha[M_2]}{r_1}} \tag{9}$$

The results are reported in Tables 3 and 4.

The values of ρ which have been obtained at -10 and -30°C follow the classical relation

$$\frac{d \ln \rho}{dT} = \frac{\Delta H}{RT^2}$$

which enables us to calculate ΔH. The value obtained is $\Delta H = -15 \pm 3$ kcal/mol which is in agreement with the values we determined by classical calorimetric measures [7]: -15 ± 1 at -70°C and -18 ± 0.7 at -30°C.

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TABLE 3. Values of α and ρ Obtained for Different Specific Monomer Concentrations at -10°C; "r_1" (See Text) = 5.54; r_2 = 1.10[a]

$[M_1]$	$[M_2]$	α	ρ	$\frac{\alpha}{[M_1]}$
0.03	0.07	0.43	20.4	14.3
0.04	0.06	0.58	22.5	14.5
0.05	0.05	0.66	23.1	13.6
0.06	0.04	0.77	21.6	12.8
0.07	0.03	0.81	16.7	11.6

[a] Average value of $\rho:\bar{\rho}$ = 20.9.

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TABLE 4. Values of α and ρ Obtained for Different Specific Monomer Concentrations at -30°C; "r_1" (See Text) = 4.53, r_2 = 0.80[a]

$[M_1]$	$[M_2]$	α	ρ	$\frac{\alpha}{[M_1]}$
0.03	0.07	0.65	252	21.7
0.04	0.06	0.74	320	18.5
0.05	0.05	0.81	257	16.2
0.06	0.04	0.86	196	14.3
0.07	0.03	0.91	130	13

[a] Average value of $\rho:\bar{\rho}$ = 231.

Activation Enthalpy and Entropy Values

From Figs. 1 and 2 the following activation enthalpy and entropy values can be obtained.

For the system 1-vinyl naphthalene-styrene:

$$\Delta H_{22}^{\neq} - \Delta H_{21}^{\neq} = 1.20 \text{ kcal/mol}$$

$$\Delta H_{11}^{\neq} - \Delta H_{12}^{\neq} = 1.06 \text{ kcal/mol}$$

$$\Delta S_{22}^{\neq} - \Delta S_{21}^{\neq} = 4.58 \text{ cal/mol/K}$$

$$\Delta S_{11}^{\neq} - \Delta S_{12}^{\neq} = 7.50 \text{ cal/mol/K}$$

For the system 2-vinyl naphthalene-styrene:

$$\Delta H_{22}^{\neq} - \Delta H_{21}^{\neq} = 0.66 \text{ kcal/mol}$$

$$\Delta H_{11}^{\neq} - \Delta H_{12}^{\neq} = 0.62 \text{ kcal/mol}$$

$$\Delta S_{22}^{\neq} - \Delta S_{21}^{\neq} = 3.4 \text{ cal/mol/K}$$

$$\Delta S_{11}^{\neq} - \Delta S_{12}^{\neq} = 5.3 \text{ cal/mol/K}$$

These results show that 1-vinyl naphthalene is more reactive than 2-vinyl naphthalene and that the selection of the two monomers by the cation is enthalpically controlled for the 2-vinyl naphthalene-styrene system and entropically controlled for the 1-vinyl naphthalene-styrene system. A general discussion of that phenomenon and its correlation with quantum chemistry is given in another work [16].

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REFERENCES

[1] P. Belliard and E. Marechal, Bull. Soc. Chim. Fr., p. 4662 (1972).
[2] S. Cohen, P. Belliard, and E. Marechal, Polymer, p. 352 (1973).
[3] W. J. Cho, C. Bunel, and E. Marechal, J. Polym. Sci., Polym. Chem. Ed., In Press.
[4] C. Bunel, S. Cohen, J. P. Laguerre, and E. Marechal, Polym. J., 7, 320 (1975).
[5] J. Coudanne and E. Marechal, C. R. Acad. Sci., 286c, 169 (1978).
[6] P. Blin, C. Bunel, and E. Marechal, J. Chem. Res., S, 206; M, 2619 (1978).
[7] C. Bunel and E. Marechal, Polym. J., 10, 371 (1978).
[8] P. Blin, C. Bunel and E. Marechal, J. Polym. Sci., Polym. Chem. Ed., In Press.
[9] E. Berger, Bull. Soc. Chim. Fr., p. 338 (1906).
[10] W. Davis and Q. N. Porter, J. Chem. Soc., p. 459 (1957).
[11] N'guyen Anh Hung, Thèse de 3ème cycle, Paris, 1970.
[12] T. Kelen and F. Tüdös, J. Macromol. Sci.–Chem., A9, 1 (1975).
[13] G. G. Lowry, J. Polym. Sci., 42, 463 (1960).
[14] H. Sawada, J. Macromol. Sci.–Rev. Macromol. Chem., 9, 235 (1973).
[15] A. V. Tobolsky and A. Eisenberg, J. Am. Chem. Soc., 82, 289 (1960).
[16] C. Bunel and E. Marechal, J. Polym. Sci., Polym. Chem. Ed., In Press.

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