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Claude Caze[a]; Claude Loucheux[a]
[a] Laboratoire de Chimie Macromoléculaire, Université des Sciences et Techniques de Lille, Villeneuve d'Ascq, France

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Mechanism of the Radical Copolymerization of Methyl Methacrylate and Maleic Anhydride

CLAUDE CAZE and CLAUDE LOUCHEUX

Laboratoire de Chimie Macromoléculaire
Université des Sciences et Techniques de Lille
B. P. 36, F 59650 Villeneuve d'Ascq, France

ABSTRACT

The kinetics of the copolymerization of methyl methacrylate and maleic anhydride was investigated in benzenic solutions at 60 and 70°C and in bulk at 60°C. The microstructure of the copolymers was determined by ^{1}H-NMR and IR spectrophotometry. In benzene solutions the mechanism of copolymerization involves the participation of an associative species between both comonomers. In bulk a terminal model is sufficient to explain all the results.

INTRODUCTION

The radical copolymerization of methyl methacrylate (MMA) and maleic anhydride (MA) has been studied [1, 2]. More recently Dogson and Ebdon [3] investigated the terpolymerization of MMA, MA, and methyl acrylate. This reaction involves a charge-transfer complex between MMA and MA. The aim of this paper is to determine the influence of such an association on the radical copolymerization of MA and MMA, by using the results of the kinetics and sequence distribution studies (in various experimental conditions).

EXPERIMENTAL

Copolymerizations were carried out in vacuum-sealed glass ampules at the desired temperature (± 0.1°C). The copolymers were precipitated in heptane and the monomer conversion did not exceed 10%. The composition of these copolymers was determined by a conductometric titration of the anhydride functions by use of tetraethylammonium hydroxide as titration reagent in pyridine. Copolymerizations were studied in benzene at 60 and 75°C and at a total monomer concentration of 2 mole/liter. Azobisisobutyronitrile (AIBN) was used as the initiator at a concentration of 5×10^{-3} mole/liter. Copolymerizations were also carried out without solvent at 60°C and with AIBN (6×10^{-3} mole/liter) as the initiator. ^{1}H-NMR spectra were obtained from pyridine solution with a Cameca TSN 250 MHz spectrometer, TMS being used as internal reference. Infrared spectra were recorded from films with a Bechman IR 18 instrument.

THEORETICAL

The r_1, r_2 copolymerization parameters (where 1 and 2 refer to MMA and MA, respectively) were determined by the method of Yezrielev et al. [4]. This method is based on Eq. (1):

$$(F/f^{1/2})r_1 + (f^{1/2}/F)r_2 + (1/f^{1/2}) - f^{1/2} = 0 \tag{1}$$

where F is the ratio of each monomer concentration in the feed ($[M_1]/[M_2]$) and f is the mole ratio of each monomer unit (m_1/m_2) in the copolymer. r_1 and r_2 were determined by the method of least squares applied to Eq. (1). The conversion rate of the monomers was corrected according to the method of Joshi [5]. In this method, the F value used is the average of the F value at zero conversion and at conversion c. This value ($\bar{F}$) was obtained from successive Eqs. (2), (3), and (4):

$$F_2^c = \frac{F_2^0 - \left\{\dfrac{[F_2^0 M_2 + (1 - F_2^0)M_1]c}{f_2 M_2 + (1 - f_2)M_1}\right\} f_2}{1 - \left\{\dfrac{[F_2^0 M_2 + (1 - F_2^0)M_1]c}{f_2 M_2 + (1 - f_2)M_1}\right\}} \tag{2}$$

where F_i^c is the mole fraction of monomer i at conversion c in feed, f_i the mole fraction of monomer i in the copolymer and M_i the molecular weight of monomer i.

$$\overline{F}_2 = (F_2^0 + F_2^c)/2 \qquad (3)$$

$$\overline{F} = (1 - \overline{F}_2)/\overline{F}_2 \qquad (4)$$

The penultimate effect in copolymerization was taken into account for Barb's treatment [6] (MA does not homopolymerize, thus $r_{22} = r_{12} = 0$) according to Eq. (5):

$$(f - 2)/\overline{F} = r_{11} - (1/r_{21})\left[(f - 1)/\overline{F}^2\right] \qquad (5)$$

The charge-transfer complex intervention was characterized by the treatment of Litt [7] (in the case of $r_2 = 0$ and with the approximation of the authors):

$$\frac{1}{[M_2](f - 1)} = \frac{1}{[M_1]}\;\frac{1}{r_{12}} + \frac{K}{r_{1c2}} \qquad (6)$$

K is the formation constant of the charge-transfer complex, defined as:

$$M_1 + M_2 \rightleftharpoons C$$

$$K = [C]/([M_1][M_2]) \qquad (7)$$

and

$$r_{1c2} = k_{11}/k_{1c2}$$

where k_{1c2} is the velocity constant of the reaction:

$$m_1^{\bullet} + c \xrightarrow{k_{1c2}} m_1^{\bullet}$$

TABLE 1. Copolymerization in Benzene at 60°C[a]

F_2^0	f_2	C	$\overline{F_2^0}$	$\overline{F}$	f
0.15	0.0658	0.142	0.157	5.367	14.20
0.30	0.126	0.085	0.308	2.246	6.94
0.40	0.166	0.069	0.409	1.447	5.04
0.50	0.198	0.105	0.518	0.930	4.05
0.60	0.235	0.103	0.621	0.610	3.26

[a] AIBN = 5×10^{-3} mole/liter; total monomer concentration = 2 mole/liter.

RESULTS AND DISCUSSION

Copolymerization in Benzene at 60°C

The results are reported in Table 1. The terminal model gives $r_1 = 2.39 \pm 0.02$, $r_2 = -0.165 \pm 0.008$. r_2 has a negative value; thus the terminal model does not agree. The r_{11}, r_{21} parameters defined in the penultimate model were determined by Eq. (5) as shown in Fig. 1. We obtained $r_{11} = 2.24$, $r_{21} = 36.5$. The value of the r_{21} parameter is too high to be compatible with a penultimate effect. Figure 2 shows a plot of $\{[M_2](f - 1)\}^{-1}$ versus $[M_1]^{-1}$. We obtained $r_{21} = 6.15$ and $(K/r_1c_2) = 0.15$. The order of magnitude of these values agrees with a charge-transfer model.

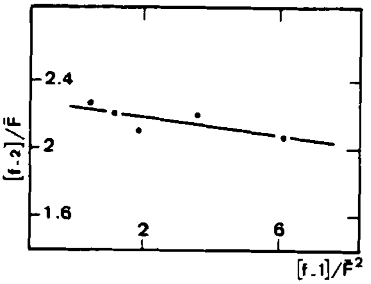

FIG. 1. Penultimate analysis of data of the copolymerization in benzene at 60°C.

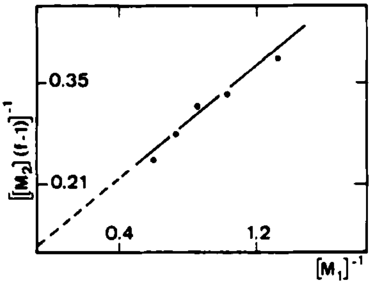

FIG. 2. Charge transfer analysis of data of the copolymerization in benzene at 60°C.

TABLE 2. Copolymerization in Benzene at 75°C[a]

F_2^0	f_2	C	$\overline{F_2^0}$	$\overline{F}$	f
0.15	0.0628	0.101	0.153	5.536	14.92
0.30	0.1206	0.083	0.307	2.257	7.29
0.40	0.134	0.120	0.409	1.445	6.46
0.50	0.191	0.072	0.512	0.953	4.23
0.60	0.224	0.098	0.608	0.645	3.46

[a] AIBN = 5×10^{-3} mole/liter; total monomer concentration = 2 mole/liter).

Copolymerization in Benzene at 75°C

This system has been studied by Smets et al. [8], who obtained values of $r_1 = 6.7$ and $r_2 = 0.02$. Our results are reported in Table 2. The terminal model gives $r_1 = 2.5 \pm 0.1$, $r_2 = -0.22 \pm 0.04$. As for the results obtained in the copolymerization at 60°C, r_2 is negative, excluding the terminal model. Figure 3 shows the variation of $(f - 2)/\overline{F}$ versus $(f - 1)/\overline{F}^2$. We obtain for r_{11} and r_{12} parameters characteristic of the penultimate effect the respective values 2.35 and 84. The r_{12} parameter has an impossibly high value. Figure 4 shows the determination of the charge-transfer complex model parameters. We obtain $r_{12} = 6.53$ and $K/r_{1c2} = 0.143$. These values

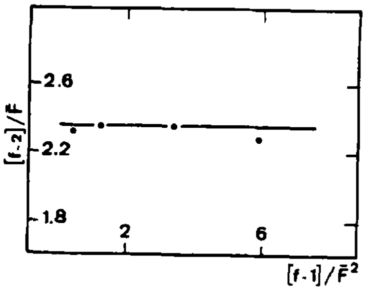

FIG. 3. Penultimate analysis of data of the copolymerization in benzene at 75°C.

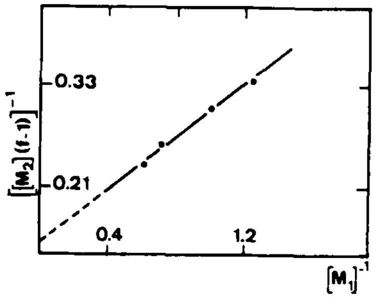

FIG. 4. Charge transfer analysis of data of the copolymerization in benzene at 75°C.

(taking into account experimental errors) are in the same range as the values obtained in the case of the copolymerization at 60°C in benzene.

Bulk Copolymerization at 60°C

This system has been studied by Melville et al. [1]. They obtained $r_1 = 3.33$ and $r_2 = 0.00$. Our results are reported in Table 3. The terminal model gives $r_1 = 3.11 \pm 0.06$, $r_2 = -0.07 \pm 0.03$. We obtain for r_2 a very small negative value. It is possible that the terminal model agrees in the case of the bulk copolymerization. Figure 5 shows $(f - 2)/\bar{F}$ versus $(f - 1)/\bar{F}^2$. We obtain for the r_{11} and r_{12}

TABLE 3. Copolymerization in Bulk at 60°C[a]

F_2^0	f_2	C	$\overline{F_2^0}$	f	$\overline{F}$
0.15	0.0540	0.038	0.151	18.45	5.622
0.30	0.1048	0.031	0.306	8.54	2.300
0.40	0.138	0.033	0.409	6.21	1.473
0.50	0.182	0.050	0.508	4.49	0.968
0.60	0.243	0.051	0.609	3.11	0.642

[a] AIBN = 6×10^{-3} mole/liter.

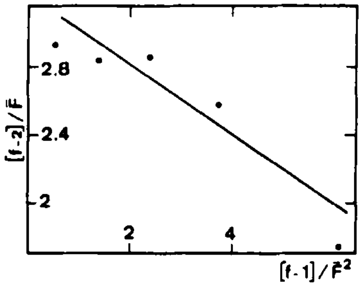

FIG. 5. Penultimate analysis of data of the copolymerization in bulk at 60°C.

parameters the respective values 3.21 and 4.12. A penultimate model gives acceptable values of the r_{11}, r_{12} parameters. A small penultimate effect would be perceptible, but the precision of the determination of r_{11} and r_{12} is not sufficient to establish the reality of the existence of such an effect. Figure 6 shows the charge-transfer complex analysis of our data: we obtain $r_{12} = 3.645$ and $K/r_1c_2 = 3 \times 10^{-2}$. It seems that K/r_1c_2 value shows that $K \simeq 0$. Of course in this case, the kinetic results do not agree with a charge-transfer complex model.

Microstructure of Copolymers

Comparison of the experimental sequence distribution and the calculated one (based on kinetic models) is a means of ascertaining the

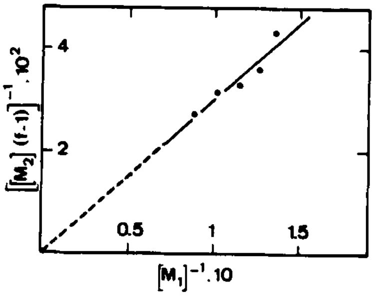

FIG. 6. Charge transfer analysis of data of the copolymerization in bulk at 60°C.

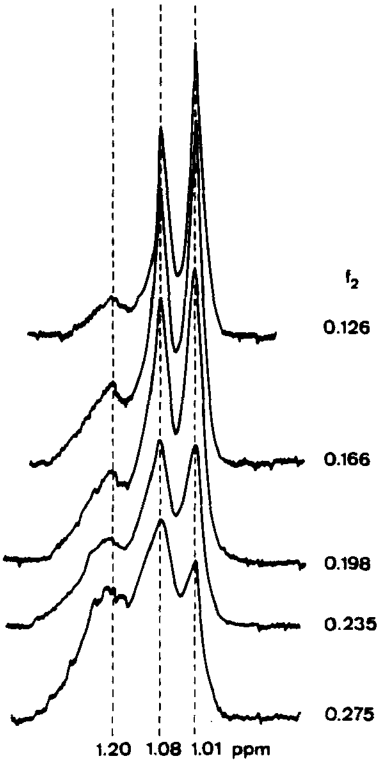

FIG. 7. Evolution of the α-CH_3 resonance vs. the mole fraction of monomer 2. Copolymerization carried out in benzene at 60°C.

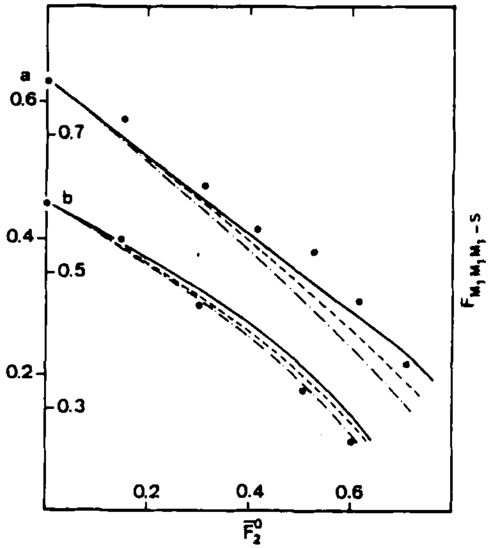

FIG. 8. Comparison of the calculated and experimental fraction of MMA unit in syndio triad configuration for (a) copolymerization in benzene at 60°C and (b) copolymerization in bulk at 60°C: (●) experimental result; (—) terminal model; (--) penultimate model; (——) charge transfer model.

reaction scheme. High resolution ^{1}H-NMR [9] and IR spectrophotometry [10] is readily available for studying the microstructure of MMA/MA copolymers.

NMR Studies

The determination of the microstructure of MMA copolymers is based essentially on the α-CH_3 resonance. Figure 7 shows the α-CH_3 resonance with increasing m_2 content in the copolymer. In the case of homopoly MMA three peaks appear at 1.01, 1.08, and 1.20 ppm, due to the resonance of syndio, hetero, and iso triads, respectively. In the case of the copolymers we observe the appearance three bands centered at 1.14, 1.20, and 1.24 ppm. Assignment of these bands cannot be made, since we observe not only the influence of the sequence distribution but also that of the tacticity and cotacticity. Nevertheless it is possible to determine the variation of the resonance

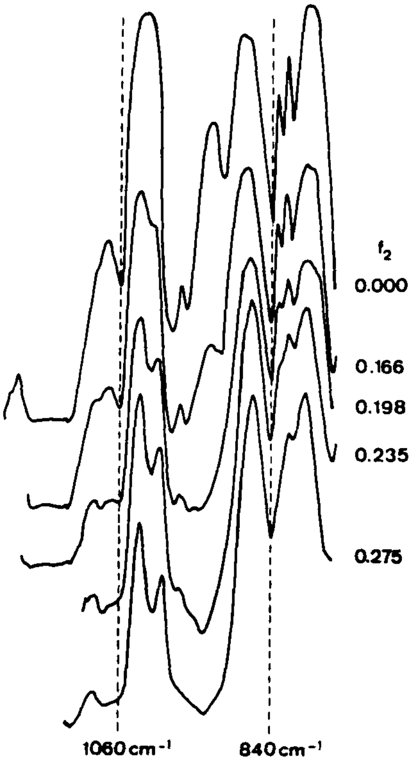

FIG. 9. Variation of the infrared spectra of copolymers with various f_2 contents (copolymerization in benzene at 60°C).

of the α-CH_3 belonging to syndio triads at 1.01 ppm. If we consider that the isotacticity parameter δ_{11} is not affected in the copolymerization process, we can calculate the fraction of MMA unit in the syndio triad configuration. Figure 8 shows this comparison in the case of copolymerization in benzene and in bulk at 60°C. Charge transfer and terminal models give the cases of solution and bulk copolymerization.

IR Studies

The band at 1060 cm^{-1} found in copolymers of MMA was assigned by Schmolke et al. [10] to the vibration of the α-CH_3 groups in

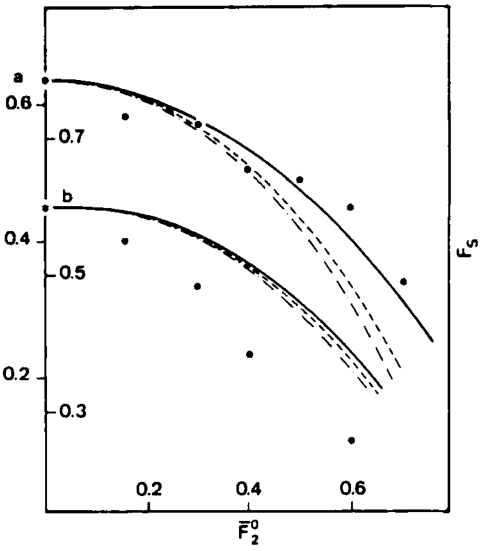

FIG. 10. Comparison of the calculated and experimental F_S for (a) copolymerization in benzene at 60°C and (b) copolymerization in bulk: (●) experimental result; (-) terminal model; (--) premultimate model; (——) charge transfer model.

syndiotactic configuration of long m_1 sequences (greater than three units). This band appears in our MMA-MA copolymers as shown in Fig. 9, and its intensity (compared with the intensity of the 840 cm^{-1} band characteristic of the m_1 units also, but independent of the configuration), decreases when the percentage of m_2 units in the copolymer increases. Using the Schmolke assumption, the fraction of α-CH_3 groups in syndiotactic configuration was plotted in Fig. 10 against the m_2 content in the copolymers and compared to the calculated value in the case of the copolymerization at 60°C. As in the NMR studies the best fit is obtained with charge-transfer and terminal models, respectively, in the cases of solution and bulk copolymerization.

CONCLUSION

Kinetic and configuration studies show that in solution the copolymerization involves the participation of an association species between the comonomers. In bulk copolymerization, a terminal model is convenient to describe the experimental results. The concentration of the complex between the comonomers is governed by Eq. (7). Theoretically, in bulk the concentration of the complex should be greater than in solution. We observe in the copolymerization results the inverse effect. We think that the K value decreases when the dielectric constant increases: an increase of MA content induces an increase of the dielectric constant of the solution and therefore a decrease of K. In bulk this phenomenon is predominant; therefore the concentration of the associative species is smaller than in solution and its effect negligible.

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