THE COPOLYMERIZATION OF PHENYL METHACRYLATE WITH METHACRYLIC ACID*

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Copolymers of methacrylic acid with its esters are used as models in the hydrolysis study of the respective polymethacrylates [1]. The knowledge of copolymerization constants r_1 and r_2 permits the calculation of the acid and ester unit distribution in the copolymer chains. In this event the kinetic study of the hydrolysis of copolymer samples enables a qualitative assessment to be made of the effect of the carboxyl group on adjacent ester bond reactivities. Values r_1 and r_2 must be known with sufficient accuracy or the percent probability must be objectively assessable. These requirements are taken into account in the modern determination methods of the copolymerization constants [2, 3], which make use of mathematical statistics.

Let us say that r_1^j and r_2^j are the jth determinations of constants r_1 and r_2. Tidwell and Mortimer [3] examined the function

$$G_i^j = G(M_2, r_j^1, r_2^j) = (r_2^j M_2^2 + M_2 M_1)/(r_2^j M_2^2 + 2M_1 M_2 + r_1^j M_1^2),$$ (1)

n which M_2 and M_1—molar fractions of copolymers in the original mixture. Every ith test in a series of n tests will give an experimental second-monomer molar fraction m_{2i} present in the copolymer, which will be approximated by

$$m_{2i} \approx G_i^j + (\partial G_i^j / \partial' r_1)(\hat{r}_1 - r_1^j) + (\partial G_i^j / \partial r_2)(\hat{r}_2 - r_2^j),$$ (2)

$\hat{r}_1^0$ and $\hat{r}_2^0$ are the mathematically expected r_1^j and r_2^j.

By making $d_i = m_{2i} - G_i^j$, $b_1 = r_1^0 - r_1^j$, and $b_2 = r_2^0 - r_2^j$, we get from eqn. (2) that

$$d_i = b_1 \partial G_i^j / \partial r_1 + b_2 \partial G_i^j / \partial r_2.$$ (3)

The Box modification of the integration method [4] is used subsequently to find r_1 and r_2, which minimizes the sum $\sum_{i=1}^{n} (d_i)^2$. Computations of the sums $S_h = [\sum_{i=1}^{n} (d_i)^2]_h$ are made $r_1 = r_1^j + [(h-1)/2]\hat{b}_1$ and $r_2 = r_2^j + [(h-1)/2]\hat{b}_2$, where $\hat{b}_1$ and $\hat{b}_2$ are parameters b_1 and b_2 for eqn. (3), found by the method of least squares, and $h = 1,2,3$. One then calculates the values $V = 1/2 + (S_1 - S_3)/[4(S_1 - 2S_2 + S_3)]$ and $S_4 = [\sum_{i=1}^{n} (d_i)^2]_4$ for $r_1 = r_1^j + V\hat{b}_1$ and $r_2 = r_2^j + V\hat{b}_2$. The calculation is repeated if $S_4 < S_1$, taking $r_1^{j+1} = r_1^j + V\hat{b}_1$, $r_2^{j+1} = r_2^j + V\hat{b}_1$. (Should $S_4 > S_1$, V is recalculated by dividing b_1 and b_2 by $\frac{1}{2}$). Two to three series will suffice to find the most probably copolymerization constants $\hat{r}_1$ and $\hat{r}_2$, minimizing the sum $\sum_{i=1}^{n} (d_i)^2$.

Furthermore, Tidwell and Mortimer were able to show that $\hat{r}_1$ and $\hat{r}_2$ can be satisfactorily determined in tests made with two specific compositions of monomer mixtures (M_{21} and M_{22}), so that determination errors of these constants will be minimal. The test should be planned as follows: any method is used at the start to get approximate r_1- and r_2-values. This pair of values and the Table given by the authors [3] are used to select the optimal monomer mixture compositions M_{21} and M_{22}. Several tests are then made at these compositions and $\hat{r}_1$ and $\hat{r}_2$ are calculated as described before.

The work described here dealt with the copolymerization of phenyl methacrylate (PMA) with methacrylic acid (MAA) in benzene, and also in benzene–dimethylformamide (DMF) mixtures. The approximate r_1- and r_2-values were determined by the Fineman–Ross method [5]. The subsequent tests and calculations were those described before [3].

EXPERIMENTAL

The MAA was freeze-dried 2 or 3 times and then vacuum-distilled at 63–65°C/15 mm in a nitrogen stream over calcium hydride; n_D^{20} 1·4330. The methacrylyl chloride was synthesized from MAA and thionyl chloride [6]; b.p. 95–96°C/760 mm, n_D^{20} 1·4420. The PMA was produced from methacrylyl chloride and phenol [7]; its constants were as follows: b.p. 83–84°C/4 mm, n_D^{20} 1·5145. Benzoyl peroxide (BP) was purified by recrystallization (from chloroform solution, by adding methanol); the benzene and DMF were dried by the customary methods.
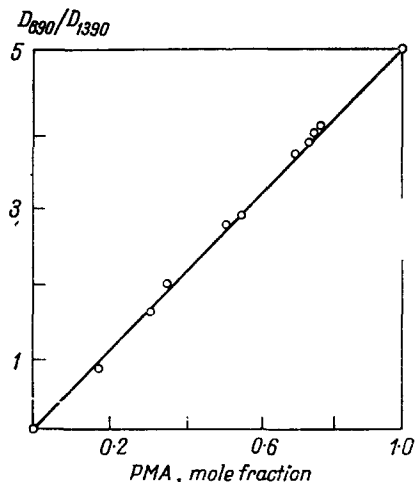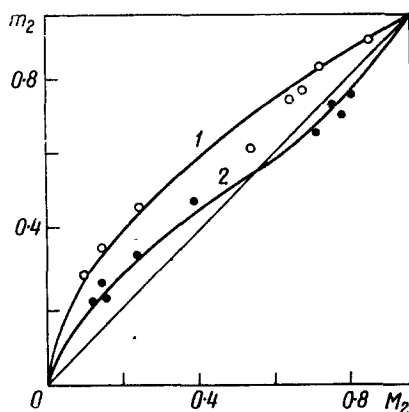

FIG. 1

FIG. 2

FIG. 1. The optical density ratio D_{690}/D_{1390} as a function of the poly-PMA–poly-MAA mixture composition.

FIG. 2. The copolymer composition as a function of the monomer mixture composition; 1—copolymerization in benzene–DMF mixtures, 2—in benzene.

Ampoules were used for the copolymerization at 60°C and the % conversion was small. The solvent was benzene or its mixture with DMF; the monomer mixture made up 20% v/v of the solution. A 3 : 1 molar ratio of DMF : MAA was maintained in all cases, because the MAA reactivity depended on this ratio in the copolymerization [8].

The copolymers produced in benzene were soluble in a methylethylketone/methanol mixture (varying in composition as a function of the copolymer composition), and sedimented out in petroleum ether. A homogeneous solution was obtained in tests with DMF additions, from which the copolymer was precipitated with petroleum ether. The samples were purified by double precipitation with an MEK/methanol solution, and then vacuum-dried at 50°C.

The copolymer compositions were determined by infrared spectroscopy, using a double beam UR-20 spectrometer with the fourth slit programme. The samples were tabletted with KBr in a ratio of 1 : 125. The composition was estimated from the characteristic absorption line ratio of the phenyl ($\nu = 690$ cm^{-1}) and methyl ($\nu = 1390$ cm^{-1}) groups. A preliminary study had been made of the dependence of the optical density ratio D_{690}/D_{1390} on the composition of artificial homopolymer mixtures of MAA and PMA. As Fig. 1 shows, D_{690}/D_{1390} was a linear function of the PMA molar fraction present in the mixture. This fraction, m_2, was thus calculated from

$$m_2 = D_{690}/D_{1390} \times 5 \cdot 1 \ .$$

Some of the copolymer sample compositions were also determined by the NSR method. The samples were methylated for this purpose with diazomethane [9] (as no universal solvent was available for copolymers of varying composition), so that the actual PMA–MMA composition could be determined. The spectra of 15% solutions in dichlorobenzene were recorded on spectrometer S-60, working with a 60 Mc/s frequency at 130–150°C, measuring the peak area ratio of the respective methoxy group protons to that of the sum of the peak areas of methylene and α-methyl group protons. There was good agreement between the results obtained by infrared spectroscopy and by NSR. The PMA content of the samples produced in tests 11/1 and 11/3 was thus 93 and 91 respectively, and 63 and 62 mole % by infrared spectroscopy and NSR.

RESULTS

The results of the MAA copolymerization with PMA (M$_2$) in the presence of DMF are shown in Table 1. The preliminary test series by the Fineman–Ross method gave constants $r_1^1 = 0 \cdot 25$ and $r_2^1 = 1 \cdot 15$. It had been stated [3] that these values are equivalent to the following optimal monomer mixture compositions: $M_{21} = 0 \cdot 6455$, $M_{22} = 0 \cdot 1050$. The ampoules containing the monomer mixture solutions of this composition (tests 7–11 in Table 1) were placed in the thermostatted oven in random order. The corrected results for $\hat{r}_1$ and $\hat{r}_2$ after calculation are

TABLE 1. MAA COPOLYMERIZATION WITH PMA (M$_2$) IN DMF

(60°C, DMF : MAA = 3 : 1 (molar), 20% v/v monomer mixture, $0 \cdot 825 \times 10^{-2}$ mole/l. BP)

Test No.	M$_2$ Content of monomer mixture	Benzene, % v/v	Conversion, % v/v	Copolymer composition, m$_2$	Test No.	M$_2$ Content of monomer mixture	Benzene, % v/v	Conversion, % v/v	Copolymer composition, m$_2$
1	0·87	76·0	5·5	0·93	7	0·65	67·2	3·8	0·74
2	0·73	70·8	5·2	0·85	8	0·10	34·1	5·1	0·29
3	0·55	60·3	6·6	0·63	9	0·10	34·1	5·1	0·30
4	0·25	46·0	5·5	0·47	10	0·65	67·2	3·8	0·78
5	0·15	39.1	5·1	0·37	11	0·65	67·2	4·5	0·76
6	0·68	68·3	5·2	0·78					

TABLE 2 CALCULATION OF $\hat{r}_1$ AND $\hat{r}_2$ FOR TEST SERIES NO. 7–11

$(r_1^1 = 0.25;\ r_2^1 = 1.15)$

Test No.	M_1	M_2	m_2	First approximation			Second approximation		
				$10^2\,(d)$	$\partial G^1/\partial r_1$	$10^2\,\partial G^{11}/\partial r_2$	$10^2\,(d)$	$\partial G^2/\partial r_1$	$10^2\,\partial G^2/\partial r_2$
7	0.3545	0.6455	0.775	4.4124	−0.095165	11.5677	0.7507	−0.088387	8.8392
8	0.8950	0.1050	0.295	2.8955	−0.531597	2.0185	+0.6030	−0.658909	2.1057
9	0.8950	0.1050	0.300	3.3955	−0.531597	2.0185	+0.1030	−0.658909	2.1057
10	0.3545	0.6455	0.765	3.4124	−0.095165	11.5677	+0.2493	−0.088387	8.8392
11	0.3545	0.6455	0.775	4.4124	−0.095165	11.5677	0.0006	−0.658909	2.1057
$\Sigma\,(\partial G^{j}/\partial r_1)^2$					0.592358			0.891758	
$\Sigma\,(\partial G^{j}/\partial r_2)^2$					+0.040959			0.024325	
$\Sigma\,(\partial G^{j}/\partial r_1)\,(\partial G^{j}/\partial r_2)$					−0.054484			−0.051189	
$\Sigma\,(\partial G^{j}/\partial r_1)d$					−0.045088			−0.003545	
$\Sigma\,(\partial G^{j}/\partial r_2)d$					+0.007049			0.000958	
$\Sigma\,(d^2)$					−0.047290			0.000155	
b_1					0.313797			0.007078	
b_2					0.007049			0.054268	
S_1					0.001933			0.000155	
S_2					0.000162			0.000098	
S_3					1.014723			0.000079	
V					0.000155			1.000000	
S_4					0.202014			0.000079	
r_1^{j+1}					1.468477			0.209092	
r_2^{j+1}								1.522685	

TABLE 3. MAA COPOLYMERIZATION WITH PMA (M₂) IN BENZENE

(60°C, 20% v/v monomer mixture, 0.825×10^{-2} mole/l. BP)

Test No.	M_2 content of monomer mixture	Conversion, % w/w	Copolymer composition, m_2	Test No.	M_2 content of monomer mixture	Conversion, % w/w	Copolymer composition, m_2	Test No.	M_2 content of monomer mixture	Conversion, %w/w	Copolymer composition, m_2
1	0·73	6·0	0·67	6	0·77	1·8	0·75	11	0·82	5·2	0·77
2	0·15	2·6	0·27	7	0·77	2·7	0·75	12	0·13	6·5	0·22
3	0·80	4·5	0·72	8	0·16	3·8	0·24	13	0·82	5·5	0·77
4	0·40	5·1	0·49	9	0·13	6·0	0·20	14	0·13	4·0	0·25
5	0·25	8·0	0·35	10	0·82	6·2	0·78				

given in Table 2, which shows that two approximations were sufficient; value $\sum(d)^2$ became smaller by a factor of 45 after the first approximation, and only by a factor of 2 after the second. (Let as compare $\sum(d)^2$ with S_4 in the second approximation; the latter would be used as $\sum(d)^2$ in a third approximation). It is easy to find the 95% confidence limits for a "two-point" test series [3] and to determine the maximal deviation of r_1 and r_2 from the most probable values.

The copolymerization constants of the process in benzene–DMF at a 0·95 probability had the following values: $r_1 = 0.21 \pm 0.02$; $r_2 = 1.52 \pm 0.13$. Figure 2 shows that the copolymer composition curve plotted for these (curve *1*) agreed well with the experimental findings.

Table 3 lists the results of the copolymerizations in benzene. The constants found by the Fineman–Ross approximation were $r_1^1 = 0.30$, $r_2^1 = 0.45$.

The results of the two-point test series (9–14, Table 3) were used to calculate the adjusted copolymerization constants of PMA and MAA in benzene; these were $r_1 = 0.40 \pm 0.14$ and $r_2 = 0.59 \pm 0.17$. The copolymer composition curve plotted from these values (Fig. 2, curve *2*) agreed well with the experimental.

We thus see that the relative reactivity of MAA in DMF decreased, while that of PMA increased. DMF and other electron-donating additions had earlier also been found to have this effect on MAA copolymerization [8, 10].

We wish to point out in conclusion that the copolymerization constants of MAA and PMA in benzene–DMF mixtures are more promising values, because in this system the process takes place under homogeneous conditions.

CONCLUSIONS

The copolymerization constants of methacrylic acid and phenyl methacrylate were determined for the process in benzene ($r_1 = 0.40 \pm 0.14$, $r_2 = 0.59 \pm 0.17$), and in a benzene–DMF mixture, using a 3:1 molar ratio of DMF to methacrylic acid ($r_1 = 0.21 \pm 0.02$, $r_2 = 1.52 \pm 0.13$).

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STUDY OF THE THERMAL DEGRADATION OF SOME POLYOLEFINS BY PYROLYTIC GAS CHROMATOGRAPHY*

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RECENT articles in the literature [1–3] reported the determination of the composition and structure of polymeric materials by pyrolytic gas chromatography (PGC), although there is still little known about the thermal degradation of polyolefins having different structures.

We used PGC to study the following polyolefins synthesized by us over chromium oxide as catalyst: polyethylene (PE), atactic and isotactic polypropylene (a-PP and i-PP), the propylene–ethylene block copolymer [4, 5].

EXPERIMENTAL

The PE was synthesized in a glandless autoclave under the following conditions: 130°C, 35 atm, 0·07% w/w catalyst content [5].

The diffractograms of the PE block copolymer and of the statistical propylene–ethylene copolymer, synthesized over chromium oxide, are compared in Fig. 1, which shows that the block copolymers had a distinct combination of two structures, i.e. that of PE with PP. Please note that the melting thermograms of the crystalline block copolymer also had 2 distinct melting peaks.