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Differential and Integral Form of Copolymerization Equation. I. Copolymerization System Vinyl Chloride/2-(Octanoyloxy)ethyl Acrylate

Jaroslav Burda^a; Olga Pádová^a; Rudolf Luká^a

^a Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Prague, Czech Republic

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DIFFERENTIAL AND INTEGRAL FORM OF COPOLYMERIZATION EQUATION. I. COPOLYMERIZATION SYSTEM VINYL CHLORIDE/ 2-(OCTANOYLOXY)ETHYL ACRYLATE

JAROSLAV BURDA,* OLGA PŘÁDOVÁ, and RUDOLF LUKÁŠ

Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
162 06 Prague 6, Czech Republic

ABSTRACT

The suspension copolymerization of vinyl chloride with 2-(octanoyloxy)ethyl acrylate was investigated. The experimental data obtained were treated using differential and integral forms of the copolymerization equation. For the solution of the integral equation, a computation program, consisting of the optimization of the copolymerization parameters by simplex method and employing the criterion of the sum of the least-square deviations, was developed. The sums-of-square deviations of individual variables were determined using the Newton method. The copolymerization parameters obtained by different methods are compared, and the methods used are discussed.

INTRODUCTION

A common plasticization of poly(vinyl chloride) (PVC) most frequently employs low-molecular-weight plasticizers which, however, easily migrate from the product. As a direct consequence of plasticizer migration, the product properties deteriorate and the environment is contaminated with the plasticizer eliminated.

The most effective solution of the problem of plasticizer migration can be seen in the production of an internally plasticized resin in which the plasticization part is

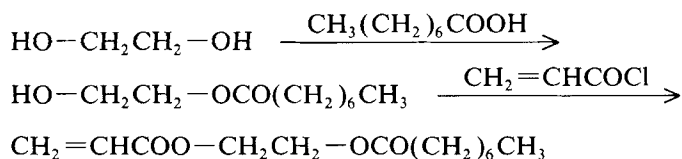
chemically bound into PVC. The class of octanoyloxyalkyl acrylates was originally invented [1, 2] to be used for internal plasticization because these comonomers possess a strong plasticization effect after their incorporation into PVC chains during copolymerization with vinyl chloride. Thus, 2-(octanoyloxy)ethyl acrylate, which is the cheapest comonomer of this class, exhibits about 80–85% of the plasticization effect of commonly used dioctyl phthalate.

However, acrylates, in general, are more reactive in the copolymerization process than vinyl chloride and, hence, to produce a more homogeneous product in structure, the dosage of the acrylate during copolymerization should be based on knowledge of the monomer reactivity ratios. In this work we focus on obtaining experimental data from the copolymerization of vinyl chloride with 2-(octanoyloxy)ethyl acrylate. The copolymerization parameters were determined using both the differential and integral forms of the copolymerization equation.

EXPERIMENTAL

Materials

Comonomer 1. 2-(Octanoyloxy)ethyl acrylate (purity 99%) was prepared by the two-step esterification of ethylene glycol [1] using octanoic acid first and then acryloyl chloride according to the following scheme:



Comonomer 2. Vinyl chloride (Spolana, Neratovice), impurities content 90 ppm at most (H₂O 65 ppm, methyl chloride 9 ppm, vinyl acetylene 6.5 ppm, 1,3-butadiene 5 ppm, ethyl chloride 4 ppm, iron < 0.5 ppm).

Initiator. Dicycyl peroxydicarbonate (Kema-Nord, Stockholm), peroxide content 73.5%, active oxygen content 2.2%.

Suspension agent. Hydroxypropyl methylcellulose (Dow Chemical Co.), viscosity of 2% aqueous solution 0.04598 Pa·s.

Copolymerization Procedure

A stainless steel reactor of the duplicator type 1 L in volume, manufactured by Ingenieurbureau SFS, Zürich, temperature control to $\pm 0.2^\circ\text{C}$, was successively charged with initiator (0.05 g), distilled water (280 mL) containing 6.0 g of suspension agent, Comonomer 1, and Comonomer 2. Total amounts of the comonomers used were 140 g; their concentrations are given in Table 1. The copolymerizations were carried out at 50°C under stirring at 400 rpm, and stopped at the chosen time intervals by cooling the reaction mixture to 15°C . After the removal of unreacted vinyl chloride, the copolymers formed were isolated by filtration, washed with a

TABLE 1. Experimental Data of Vinyl Chloride/2-(Octanoyloxyethyl) Acrylate (1) Copolymerization^a

	x_1^0	x_1	ζ
1	0.0062	0.0033	0.0472
2	0.0080	0.0046	0.0390
3	0.0120	0.0062	0.0523
4	0.0100	0.0048	0.0441
5	0.0200	0.0108	0.0528
6	0.0300	0.0174	0.0464
7	0.0400	0.0188	0.0668
8	0.0294	0.0123	0.0726
9	0.0294	0.0146	0.0911
10	0.0294	0.0132	0.1029
11	0.0294	0.0119	0.1244
12	0.0294	0.0091	0.1516

^a x_1^0 = molar fraction of Comonomer 1 in the monomer feed, x_1 = molar fraction of comonomer 1 monomeric units in the monomer mixture, ζ = mole conversion.

mixture of distilled water and methanol (1:1), extracted with hexane in a Soxhlet apparatus, and dried to constant weight.

Copolymer Composition

The content of 2-(octanoyloxy)ethyl acrylate in the copolymer was calculated from the carbon contents obtained by elemental analysis using an automatic C-H-N analyzer (Perkin-Elmer, Model 240). The results are given in Table 1.

RESULTS AND DISCUSSION

Differential Forms of Copolymerization Equation

In the mid-1940s the copolymerization equation describing in differential form the course of the copolymerization process was born [3-5], and the determination of comonomer reactivity ratios (copolymerization parameters) has become routine for polymer chemists. A simple graphic determination of the copolymerization parameters was published by Fineman and Ross [6], critically reviewed by Joshi [7], and improved by Kelen and Tüdös [8]. The graphic methods, in general, are based on the linearization of the differential form of the original copolymerization equation:

$$\frac{dM_1}{dM_2} = \frac{M_1 r_1 M_1 + M_2}{M_2 r_2 M_2 + M_1} \quad (1)$$

where M_1 and M_2 are the monomer concentrations, and $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the ratios of monomer rate constants. The expression dM_1/dM_2 describes the consumption of monomers M_1 and M_2 , and at low conversions it corresponds to the copolymer composition. Fineman and Ross [6] transformed Eq. (1) into the linear form (Eqs. 2 and 3), introducing the variables F and G :

$$G = r_1 F - r_2 \quad (2)$$

$$\frac{G}{F} = -r_2 \frac{1}{F} + r_1 \quad (3)$$

where F and G are defined as

$$F = \frac{x^2}{y} \quad \text{and} \quad G = \frac{x(y-1)}{y} \quad (4)$$

with $x = M_1/M_2$ and $y = dM_1/dM_2$.

It has been pointed out by Tidwell and Mortimer [9, 10] that data obtained under extreme experimental conditions are unequally weighted by the Fineman-Ross equations (Eqs. 2 and 3) and hence they can affect the slope of a line calculated using the linear least-squares method and the values of copolymerization parameters r_1 and r_2 obtained. Therefore, Kelen and Tüdös [8] introduced a new transformation of Eq. (1):

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (5)$$

where

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F} \quad (6)$$

The parameter α is an arbitrary constant defined by the relation

$$\alpha = \sqrt{F_m F_M} \quad (7)$$

where F_m and F_M stand respectively for the lowest and the highest value of the variable F . According to the results achieved in testing both procedures, the values of copolymerization parameters r_1 and r_2 calculated using the Kelen-Tüdös approach correspond to the best straight line obtained by the graphic method of evaluation [8].

For comparison, we also present the values obtained by the method of the "extended" Kelen-Tüdös differential equation [12]. This method includes some explicit corrections of conversion for the determination of copolymerization parameters.

For the methods based on the differential equation, the data given in Table 1 have to be converted to mole ratios and weight conversions.

Both the Fineman-Ross and Kelen-Tüdös approaches were employed in treating our experimental data of the copolymerization system vinyl chloride/2-(octanoyloxy)ethyl acrylate, and the values obtained for copolymerization parameters r_1 and r_2 are compiled in the upper part of Table 2 together with error estimations.

TABLE 2. The Values of Copolymerization Parameters Obtained by the Fineman-Ross, Kelen-Tüdös, and Integral Methods

	F-R	K-T	Extended K-T	Integral
r_1	12.9 ± 20.1 ^a	12.35 ± 17.4 ^a	8.65 ± 24.4	2.07 ± 1.12
r_2	0.084 ± 0.023 ^a	0.084 ± 0.022 ^a	0.056 ± 0.018	0.068 ± 0.002
r_1	2.12 ± 0.42	2.11 ± 0.38	2.15 ± 0.35 ^b	2.30 ± 0.15
r_2	0.38 ± 0.12	0.39 ± 0.12	0.38 ± 0.11 ^b	0.40 ± 0.06

^aDetermined using the experimental data at $\zeta < 0.07$.

^bValues published in Reference 12.

The copolymerization parameters calculated by the Fineman-Ross and Kelen-Tüdös linear graphic methods are based only on low-conversion experimental data ($\zeta < 0.07$).

Integral Form of Copolymerization Equation

As mentioned above, the use of the differential copolymerization equation in determining the copolymerization parameters is limited to low conversion experimental data. As the copolymerization proceeds to higher conversion degrees, the error in the determination of copolymerization parameters increases, eventually making the values obtained worthless. Since we were interested to learn more about the behavior of the copolymerization system at higher conversions, our experimental data for various conversion degrees were treated using the integral form of the copolymerization equation originally derived by Meyer [11]:

$$\zeta = 1 - \left(\frac{x_1}{x_1^0} \right)^\alpha \left(\frac{x_2}{x_2^0} \right)^\beta \left(\frac{x_1^0 - \delta}{x_1 - \delta} \right)^\gamma \quad (8)$$

where $\zeta = -M/M^0$ is the degree of conversion, $M = M_1 + M_2$ is the sum of moles of monomers after reaction, M^0 is the sum of moles of monomers before reaction, x_1 is the molar fraction of the first monomer, and the constants α , β , γ , and δ are defined as follows: $\alpha = r_2/(1 - r_2)$, $\beta = r_1(1 - r_1)$, $\gamma = (1 - r_1 r_2)/(1 - r_1)(1 - r_2)$, $\delta = (1 - r_2)/(2 - r_1 - r_2)$.

For the solution of Eq. (8) a computational program, consisting of the optimization of copolymerization parameters by the simplex method and employing the criterion of the sum of the least-square deviations, was developed. This criterion was applied to the variables x_1 , x_1^0 , and ζ . The determination of the least-squares deviations of ζ is accessible by direct computation if experimental data on the composition of the copolymerization mixture before and after reaction are introduced. The sums-of-square deviations of the variables x_1 and x_1^0 were determined by solving the implicit function (9), derived from the Eq. (8), by the Newton method:

$$x^{\alpha/\gamma} (1 - x)^{\beta/\gamma} + k_1^{1/\gamma} x + k_2^{1/\gamma} = 0 \quad (9)$$

where x is the searched variable x_1^0 or x_1 , and the constants k_1 and k_2 are defined by Eqs. (10) and (11):

$$k_1 = \frac{b^\alpha(1-b)^\beta}{(b-\delta)^\gamma}(1-\zeta)^{\alpha\gamma} \quad (10)$$

and

$$k_2 = -k_1\delta \quad (11)$$

The variable b is the experimentally determined complementary component to the variable x ; for the variables x_1^0 and x_1 , a equals -1 and 1 , respectively.

In differential approaches, all methods lead to linear regression and both standard deviations and error estimations are determined in a common way. Our treatment is based on a nonlinear regression. Therefore we decided to estimate the standard deviation by using the following procedure: From the set of experimental data (Table 1), we gradually omitted one input line and, in this way, we obtained 12 different pairs of r_1 and r_2 . Then we treated these pairs by employing the standard statistical tools, which enabled us to get the standard deviation of the calculated copolymerization parameters.

By comparing all obtained deviations, it can be seen that the system under study suffers from a big error in the determination of parameters r_1 and r_2 , independently of the method used. In all likelihood this is caused by the fact that the described system appears to be very complex, especially if the great differences in the reactivities of comonomers are considered. Such a system may not meet the conditions for which the entire theoretical model is valid. The difficulty of uncertainty in receiving reliable experimental data can be demonstrated by the fact that the data given on Line 11 of Table 1 have to be omitted from the analysis by the extended Kelen-Tüdös method [12] because these data are out of the definition range for this method ($\zeta_1 > 1$). It is interesting how much the copolymerization parameters are affected by the chosen method, in spite of the fact that a conversion of 15% does not seem to be too high. Moreover, if the error estimation is considered, one can see that the approach based on the treatment using the integral equation gives more reliable results.

To support this opinion, we tried to evaluate the system of comonomers 1,3-dioxolane/styrene published in Reference 12 in the same way. The results are given in the lower part of Table 2. It is obvious that in this nonproblematical case of copolymerization, the values of copolymerization parameters and their error estimation exhibit the same trends as in our case (Table 2, upper part).

This fact justifies, or at least supports, application of the integral equation for handling middle and high conversion data.

CONCLUSIONS

The determination of copolymerization parameters from the integral form of the copolymerization equation is more advantageous than the solution of the differential equation because the mathematical treatment is not limited to the use of low conversion experimental data. The computation program developed can be easily applied using common PC computers, and the data processing takes several

minutes of computation time. Using the values of copolymerization parameters r_1 and r_2 obtained, a program for the continuous dosage of 2-(octanoyloxy)ethyl acrylate during copolymerization was developed, and its application gave rise to a copolymer more homogeneous in composition.

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