Copolymerization Kinetics
# for 2-Isopropenyl-2-Oxazoline
(Methods and Results)

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Synopsis

The reactivity ratios for 2-isopropenyl-2-oxazoline (IPO), a dual functional monomer, have been determined using a combination of gas chromatography, with an internal standard, and a new form of the integrated copolymerization equation. The results indicate a parallel trend with the reactivity ratios of styrene in spite of the large disparity in polarity between IPO and styrene.

INTRODUCTION

Monomers which contain dual functionality have generated considerable interest because of the unique polymeric structures which can be prepared. Applications in such areas as polymeric supports and graftable polymers have been studied. One such monomer is 2-Isopropenyl-2-oxazoline (IPO), which readily copolymerizes with most commercially useful monomers via the isopropenyl group, while the oxazoline functionality is capable of both polymerization under acid catalysis and facile coupling via a ring-opening reaction with carboxylic acids.

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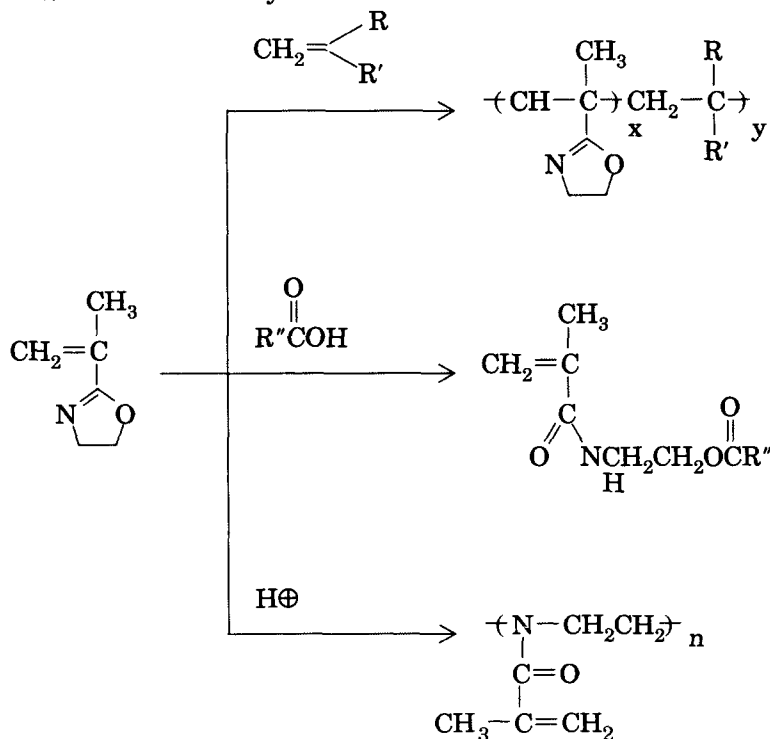
Thus, copolymers containing IPO are useful for grafting polar side chains onto hydrophobic backbones, for crosslinking with dicarboxylic acids or carboxylic acid containing copolymers, as reactive adhesives, and as hydrophilic supports for catalysts, enzymes, or reagents. In order to obtain the correct distribution of the functionality during polymerization, control of the reaction is necessary. Unfortunately, there is little information available on the copolymerization kinetics of this useful monomer. Only its copolymerization kinetics with styrene have been reported to date.[1] Thus, we undertook a study of the copolymerization kinetics of IPO with a number of other commercially interesting monomers.

EXPERIMENTAL

Materials

IPO is a developmental monomer produced by The Dow Chemical Company. All other monomers were obtained from commercial sources and purified by vacuum distillation. The internal standards for gas chromatography were gold label decane from Aldrich Chemical Co. and scintillation-grade p-xylene from J. T. Baker Co. Both were used without further purification. AIBN, 2,2'-azobis(2-methylpropionitrile), was obtained from the Aldrich Chemical Co.

Safety

IPO and acrylonitrile are highly toxic monomers which require special safety precautions. IPO can be absorbed through the skin. Thus, when working with these monomers, it was necessary to wear protective clothing to prevent skin contact. Nitrile rubber gloves, a face shield, a lab coat, and an apron were worn during all handling procedures. In addition, all operations were performed in a well-ventilated hood with an organic vapor respirator available in case of a vapor release or a spill. Residual IPO was rendered much less toxic by decomposition with 10% sulfuric acid.

Equipment

The copolymerizations were performed in 10 mL Wheaton microvials sealed with Mininert® valves and were heated in a constant temperature oil bath. The reaction vials were sampled with a 1 μm Hamilton syringe, and compositions of the reaction mixtures were analyzed on a Hewlett Packard 5710A gas chromatograph equipped with a thermal conductivity detector and a Hewlett Packard 3380A automatic integrator.

Calibration

Good calibrations for each of the components in the copolymerization mixture were obtained from 4 accurately prepared samples, each having different amounts of the two monomers and solvent. The ratios of monomers used were 10/90, 40/60, 60/40, and 90/10 by weight with the internal standard at approximately 10%. Duplicate samples were analyzed for each composition and the average value determined. The N-vinylpyrrolidone-

IPO-decane system was analyzed on a 3-ft column coated with 10% UCS-98 at 90°C and a helium flow rate of 40 mL/min. All of the other systems were analyzed on a 6 ft column coated with 10% Carbowax® 20 M at 100°C and a helium flow rate of 40 mL/min.

Copolymerizations

The copolymerization media contained the appropriate amounts of the comonomers (mole ratios of approximately 87:13 and 13:87 were used), approximately 10 mol% of an inert hydrocarbon as an internal standard, and 0.1-0.5 wt% AIBN as the initiator. The initiator was weighed into the Wheaton 10 mL vials which were subsequently sealed. Loading with monomers (5 g) and internal standard (0.5 g) was accomplished through the Miniert valve via syringe. The reactants were shaken until the AIBN had completely dissolved. This was followed by heating to the reaction temperature (Table I) in a hot oil bath. Samples were withdrawn by syringe at appropriate time intervals and analyzed by gas liquid chromatography (GLC) using the conditions listed above. The polymerizations were generally allowed to proceed until at least 15% conversion was attained. A minimum of two samples were run for each composition.

RESULTS AND DISCUSSION

The previous method for determining reactivity ratios, using the Alfrey-Mayo copolymerization equations coupled with analysis of the reaction products by isolation and purification of the resulting polymer, led to approximations of the true reactivity ratios due to large experimental errors and the methods used to handle the mathematics. Recently, a number of advances have been made which greatly improve the accuracy of the resulting reactivity ratios. High-speed computers have made it possible to analyze the integrated form of the copolymerization equations, thus taking into account the changing composition of the reaction mixture and allowing the kinetics to be followed to much higher conversions, thus reducing experimental error.

Tidwel and Mortimer[2] have shown that certain ratios of starting monomers can further improve the accuracy of the experimental results. Ger-

TABLE I
Reactivity Ratios and Reaction Temperature of Comonomers with IPO

Comonomer	Reaction temperature (°C)	r_1 (Comonomer)	σ	r_1 (IPO)	σ
Styrene	80	0.67	0.02	0.64	0.03
Ethyl acrylate	80	0.19	0.02	1.39	0.06
Methyl acrylate	60	0.16	0.04	1.90	0.08
Butyl acrylate	80	0.24	0.01	1.40	0.08
Methyl methacrylate	80	0.69	0.02	0.99	0.07
Vinyl acetate	70	0.25	0.04	7.1	2.0
N-vinylpyrrolidone	80	0.01	0.02	3.5	1.2
Acrylonitrile	70	0.13	0.04	0.52	0.06

man and Heikens[3] introduced the use of quantitative gas liquid chroma-
tography (GLC) for the analysis of the monomer composition, which reduced
errors inherent in the polymer isolation and analysis, although Petrak and
Pitts[4] have shown that this method is not without some pitfalls such as
incomplete volatilization of the monomers during GLC analysis due to the
adsorption of monomer by the polymer present in the sample. Their results
suggest that the error due to incomplete volatilization is minimal below
25% conversion. These advances have been incorporated into an analytical
procedure which entailed GLC analysis of the reaction mixtures coupled
with an internal standard to yield both composition and percent conversion
from a single sample.

The reactivity ratios were obtained from these data by an iterative so-
lution of a convenient form of the integrated copolymerization Equation (1).

$$r_2 ln \frac{X}{Xo} + (1 - r_2)ln \frac{M_2^0}{M_2} + (p + r_2)ln \frac{(Xo - P)}{(X - P)} = 0 \qquad (1)$$

where

$$p = \frac{(1-r_2)}{(1-r_1)}; \quad x = \frac{M_1}{M_2}; \quad xo = \frac{M_1^0}{M_2^0}$$

M_1^0 and M_2^0 are the initial concentrations.
M_1 and M_2 are the monomer concentrations at some finite conversion.

This equation is equivalent to the one developed by Mayo;[5] it is not valid
for the special cases $r_1 = 1$ or $r_2 = 1$. For these cases, Equations (2) and (3)
hold.

$$r_2 ln \frac{X}{Xo} + (1 - r_2)ln \frac{M_2^0}{M_2} + (X - Xo) = 0 \quad r_1 = 1 \qquad (2)$$

$$ln \frac{Xo}{X} + (1 - r_1)ln \frac{M_2^0}{M_2} + \left(\frac{1}{X} - \frac{1}{Xo}\right) = 0 \quad r_2 = 1 \qquad (3)$$

When using Equation (1), two experiments are run: one at relatively high
M_1^0 (≈ 87 mol%), where r_1 can be accurately determined, and the other at
high M_2^0, where r_2 can be accurately determined. M_1 and M_2 are deter-
mined after some conversion, and r_1 and r_2 are calculated from Eq. (1) using
an iterative computer procedure (Table I) in which r_1 is derived from the
experiments with a high mole ratio of M_1^0 and r_2 from runs with high M_2^0.

If M_1 and M_2 are expressed as concentrations, it is important to use the
same reference unit as used for M_1^0 and M_2^0. Thus, if mole fraction is used,
it is necessary to include the moles of monomer which have polymerized
when calculating M_1 and M_2.

The reactivity ratios presented in Table I are averages of multiple samples
for several copolymerization runs. Reports such as Petrak's, which indicate
that gas chromatograph methods of analysis lead to increasing errors as
the conversion increases, led us to analyze our results to determine which

TABLE II
Reactivity Ratios for IPO-Styrene versus Conversion

Conversion (%)		Reactivity ratio	
Run 1	Run 2	IPO	Styrene
7.45	5.15	0.667	0.667
10.31	5.52	0.615	0.801
10.75	9.25	0.622	0.688
20.08	22.37	0.656	0.654
23.87	22.37	0.656	0.649
34.16	22.37	0.650	0.645
37.94	25.05	0.648	0.678

conversion ranges would provide the most consistent data. Tables II and III show the reactivity ratios for IPO-styrene and IPO-butyl acrylate as a function of conversion.

Two conclusions can be drawn from these results. First, very low conversions lead to large errors. This is expected since the changes in composition are of a similar size to the inherent error in the methods of analysis. Second, high conversions, up to 42%, do not show any significant variations in the reactivity ratios from the intermediate conversion data. Thus, increased error with conversion, as proposed by Petrak and Pitts, is not apparent.

In general, the standard deviations appear to be quite good with the exception of the reactivity ratio for IPO with vinyl acetate or N-vinylpyrrolidone. For these cases, the large difference in the reactivity ratios causes the composition of the slower-reacting monomer to change very little, leading to larger errors due to the inherent experimental deviations. Greater accuracy in determining the composition of the reaction mixture would greatly reduce the error for these cases. Alternatively, numerous repetitions of the experimental runs could be performed. This would allow for the use of error analysis[6] or nonlinear least-squares fitting[7,8] to improve the accuracy of the reactivity ratios.

There is very little information in the literature with which to compare these reactivity ratios. The only reference to reactivity ratios for IPO is by Kagiya et al., who reported the reactivity ratios for styrene-IPO to be 0.49 and 0.55, respectively.[1] These values appear to be close to the values which we obtained, 0.67 and 0.64, respectively, but the differences are significant.

TABLE III
Reactivity Ratio of IPO-butyl Acrylate versus Conversion

Conversion (%)		Reactivity ratio	
Run 1	Run 2	IPO	Butyl acrylate
18.38	5.15	1.674	0.250
18.38	18.35	1.358	0.236
18.38	21.55	1.277	0.233
38.16	28.48	1.383	0.232
42.25	28.48	1.384	0.233

TABLE IV
A Comparison of Styrene versus IPO Reactivity Ratios

	Styrene r_1	Monomer r_2	IPO r_1	Monomer r_2
Ethyl acrylate	0.80	0.19	1.39	0.19
Methyl acrylate	0.75	0.20	1.90	0.16
Butyl acrylate	0.75	0.19	1.40	0.24
Methyl methacrylate	0.50	0.45	0.99	0.69
Vinyl acetate	4.50	0.25	7.10	0.25
N-vinylpyrrolidone	12.25	0.06	3.49	0.01
Acrylonitrile	0.4	0.05	0.52	0.13

Kagiya's use of the inherently less accurate methods of isolation and analysis of purified copolymer plus the use of the differential form of the copolymerization equation to interpret the data may explain the difference between their findings and those reported in this paper.

The extension of these results to additional comonomers is difficult. The use of Q and e values is precluded because of the polar nature and thus the complex interactions of IPO with any but the most nonpolar monomers. Nevertheless, we have observed that the results from this study show IPO to have reactivity ratios similar to those of styrene (Table IV). This is especially true for r_2, where the propagating chain end is from the comonomer. These numbers are nearly identical for styrene or IPO copolymerizations. Some difference is observed for r_1, where an IPO radical on the chain end reacts preferentially with IPO while a styrenic chain end is less discriminant. This may be due to the polar nature of IPO. Although the increase in r_1 for IPO versus styrene is not large, this difference is enough to eliminate azeotropic points for many of the IPO copolymerizations. In spite of these differences, it seems reasonable to use styrene reactivity ratios with monomers that have not been studied with IPO as a first approximation of the reactivity ratios between these monomers and IPO. Note that the large difference in polarity between IPO and styrene make this only a very gross approximation, especially when polar comonomers are used.

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