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Thane D. Rounsefell^a; Charles U. Pittman Jr.^a

^a Department of Chemistry, The University of Alabama University, Alabama

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Search for a Steric Penultimate Effect: Copolymerization of 2,3,4-Trimethyl-3-pentyl Methacrylate with Styrene

THANE D. ROUNSEFELL and CHARLES U. PITTMAN, JR.*

Department of Chemistry
The University of Alabama
University, Alabama 35486

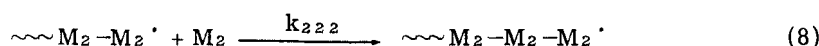
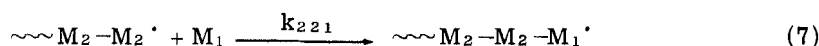
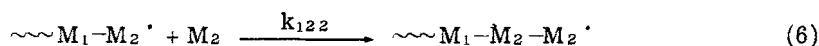
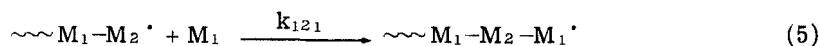
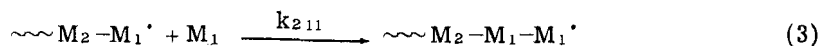
ABSTRACT

The hindered monomer, 2,3,4-trimethyl-3-pentyl methacrylate (I), was synthesized for penultimate effect studies. Since it readily homopolymerized ($k_{111} \neq 0$) and readily copolymerized with styrene, copolymerizations of I with styrene were carried out at 60°C in benzene with AIBN as initiator. The conversion to copolymer and the copolymer composition were determined by using GLC techniques. Composition-conversion data was analyzed by performing a computerized nonlinear least-squares fitting to the integrated form of the penultimate model equation. The experimental design included the use of optimized M_1^0/M_2^0 ratios. The penultimate reactivity ratios calculated from these data were $r_1' = 0.23$, $r_1 = 0.59$, $r_2 = 0.59$, $r_2' = 1.34$. Thus, when I is the penultimate unit, a terminal styryl radical prefers to add styrene, whereas when styrene is the penultimate unit, terminal styryl radicals prefer to add I. These results constitute the best evidence for a steric penultimate effect yet available in the literature from composition-conversion studies. However, the case is not yet proved. Further studies to strengthen this conclusion are proposed.

*Author to whom correspondence should be addressed.

INTRODUCTION

The penultimate model of vinyl copolymerization, first proposed by Merz, Alfrey, and Goldfinger [1] states that the next-to-last monomer unit (i.e., the penultimate unit) can influence the addition of a new monomer to the chain. The model, in its most general form, considers eight equations and four reactivity ratios which contribute to the propagation path:



where

$$r_1 = k_{111}/k_{112}$$

$$r_2 = k_{222}/k_{221}$$

$$r_1' = k_{211}/k_{212}$$

$$r_2' = k_{122}/k_{121}$$

The incorporation of monomers into the polymer is described by the penultimate copolymerization equation (9):

$$\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} = \frac{1 + r_1'[(M_1/M_2)(M_2 + r_1M_1)/(M_2 + r_1'M_1)]}{1 + r_2'[(M_2/M_1)(M_1 + r_2M_2)/(M_1 + r_2'M_2)]} \quad (9)$$

This approach was used to explain composition-conversion and sequence distribution data which did not fit the classic terminal copolymerization model [2-7]. Sequence distribution analysis has been touted to be a more sensitive probe to distinguish between terminal and penultimate models [8]. Despite the significant advances which have been made in the experimental determination [9, 10] and the calculation [11, 12] of sequence distributions, it is frequently far more difficult to obtain reliable sequence distribution data. One can conclude that in the 13 years after the Berger-Kuntz [8] assertion, no one has developed the sequence distribution analysis to the precision needed to critically test the penultimate model. Thus, it remains important to use improved methods to obtain and analyze composition-conversion data in studies of the penultimate model.

We developed an optimum computerized approach to obtain and utilize composition-conversion data to analyze the penultimate model [13, 14] and we extended a similar treatment to the charge-transfer copolymerization mechanism [14, 15]. The method involves a best nonlinear least-squares Fortran IV program for fitting the composition-conversion data. It uses Marquart's algorithm [16, 17] to speed convergence. Also, Fortran IV programs were developed [13, 14] to define the optimum experimental M_1^0/M_2^0 mole ratios to be employed in the experiments that give the composition-conversion data used in the first program. The great importance of using optimum feed ratios and the mathematical criteria for selecting these conditions have been discussed by both Behnken [18] and Box and Lucas [19]. By using a nonlinear approach, the optimum ratios are found by minimizing the area of the confidence region [20]. This is done by choosing conditions which make the determinant of the variance-covariance matrix [13, 19] as small as possible. The method is similar to that which Tidwell and Mortimer applied to the terminal copolymerization model [21, 22].

The rigorous approach developed previously [13] has never before been applied to experimental composition-conversion data in a search for a penultimate effect. Some systems which have been analyzed in terms of the penultimate model, such as styrene/maleic anhydride [2] and methyl acrylate/1,1'-diphenylethylene [23] involve large e_1 - e_2 differences. These copolymerizations, however, may also be considered in terms of the terminal-charge transfer model [14, 15, 23-25] because of the donor-acceptor relationship of the monomer pair. A good case for the existence of a steric penultimate effect has not yet

appeared. If a very bulky, yet polymerizable, monomer (M_1) was used with another "average-sized" monomer (M_2), one might expect that k_{111} [Eq. (1)] would become smaller than k_{211} . In other words, attempting to line up three M_1 units along the chain would result in steric hindrance (i. e., a buttressing effect) and, in this way, the penultimate unit, M_1 , would exhibit a steric "penultimate effect." Since a variety of acrylates and methacrylates of varying steric requirements are easily made and studied [26-32], we decided to prepare a very bulky acrylic monomer which would both homopolymerize and copolymerize to give high polymers and then analyze composition-conversion data according to the method previously described [13]. The use of two monomers, both of which would readily homopolymerize, permitted a search for the completely general case of the penultimate effect (as opposed to the special case where $k_{22} = 0$).

RESULTS AND DISCUSSION

The reactivity of various methyl α -alkylacrylates toward polystyryl radical attack has been shown [30] to follow the relation:

$$\log(1/r_1) = 0.6E_s$$

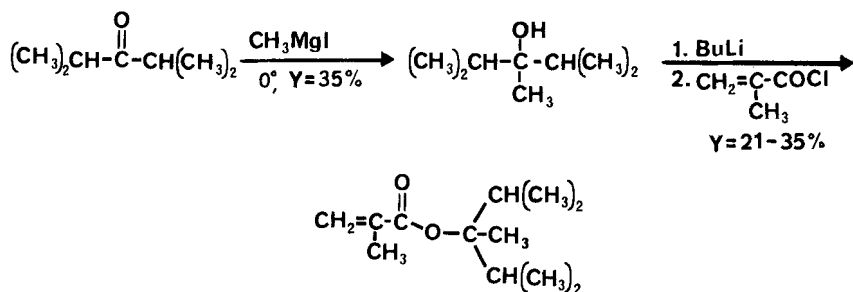
(where M_1 = methyl α -alkylacrylate), where E_s is the Taft steric constant for the alkyl group. Thus, one could consider a model monomer such as methyl α -isopropylacrylate or methyl α -tert-butylacrylate for penultimate effect studies in styrene copolymerizations. However, high polymers are only formed in the homopolymerization of methyl acrylate or methyl methacrylate. Methyl ethacrylate homopolymerizes only slowly to low polymers, and neither methyl α -isopropylacrylate nor methyl α -tert-butylacrylate homopolymerize at all (i. e., $k_{111} = 0$). For this reason, we decided to construct a methacrylate monomer with a very bulky alcohol residue, but one which would readily homopolymerize.

It is well known that methacrylates of bulky alcohols homopolymerize readily [26-29, 32]. Burnett et al. [32] concluded that k_p was constant as R increases [in $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOR}$], but that k_t decreases as a result of increased steric hindrance of the alkyl group. Later, it was concluded k_p might decrease but k_t decreased even more, so that $k_p/k_t^{1/2}$ actually increased in the series $\text{R} = \text{CH}_3 > \text{Et} > \text{Bu} > \text{iso-Bu} > \text{isobornyl}$ [27]. By making R even more bulky than isobornyl, we

postulated that k_p might be significantly reduced but that rapid homopolymerization would still occur because k_t would also decrease, leaving $k_p/k_t^{1/2}$ relatively unaffected. A very large ester function might provide a buttressing steric effect which would cause k_{111} to be reduced relative to k_{211} . Similarly, k_{121} might be reduced relative to k_{221} . For these reasons, 2,3,4-trimethyl-3-pentyl methacrylate (I) was selected for copolymerization studies with styrene.

2,3,4-Trimethyl-3-pentyl methacrylate (I) was synthesized as outlined in Scheme 1. Diisopropyl ketone was converted into 2,3,4-trimethyl-3-pentanol in 35% yield upon treatment with methyl Grignard. The lithium alkoxide was then made and reacted, in turn, with methacrylyl chloride to give monomer I in 22-35% yield. Models confirm that monomer I is reasonably hindered, and models suggest that a process which adds monomer I to $\sim M_1-M_1'$ ($M_1 = I$) would be more hindered. Monomer I was readily homopolymerized in benzene and ethyl acrylate solutions with the use of azobisisobutyronitrile as an initiator. These homopolymerizations proceeded readily at 60 and 120°C. Since the homopolymerization of I could be readily conducted at 120°C, the ceiling temperature T_c of this monomer must be substantially above 120°C. Therefore, this hindered monomer is not undergoing depropagation reactions in the copolymerization experiments with styrene (discussed later) which were carried out at 60°C. This consideration is important because it completely removes the need to consider the role of depropagation reactions in the mechanism. Thus, the treatments of such phenomena given by O'Driscoll [33, 34], Lowry [35], and others [36-39] is not germane to the work described here.

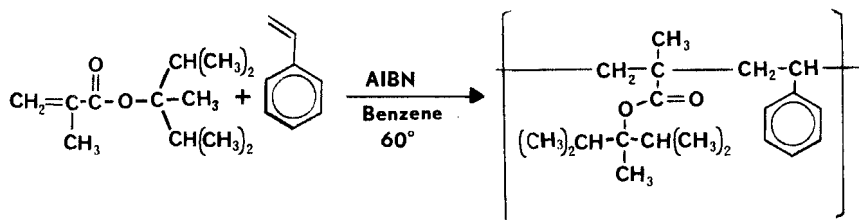
Styrene was chosen as M_2 since it is readily copolymerized with I and because it is not a hindered monomer. Furthermore, it is difficult



Scheme 1.

to see how styrene and methacrylate I could possibly form a charge-transfer complex. First, symmetry considerations and steric factors rule against this. Secondly, the e values are not too radically different. For styrene, $e = -0.80$. The value of e for I may be estimated to be between 0 and + 0.17. This estimate is based on the e values of 0.4 for methyl methacrylate and 0.17 for tert-butyl methacrylate [26].

Copolymerizations were carried out in benzene at 60°C with azobisisobutyronitrile (AIBN) as the initiator. A small amount of phenyl ethyl ether was used as an internal standard for gas-liquid chromatographic (GLC) analysis. The copolymer compositions and copolymer yields were determined by GLC analysis of the reaction solution as a function of time. By GLC, the disappearance of both monomers could be quantitatively followed by monitoring their concentration. Using this method, the incorporation of both monomers into the copolymer could be followed more accurately than by analysis of the copolymer itself. Reactions were terminated when the yields were between 5 to 10%. The feed compositions, conditions, yields, and copolymer compositions are summarized in Table 1.



Gel-permeation chromatographic analysis of the copolymers was performed on several samples to demonstrate that high molecular weights, suitable for application of copolymerization models, had been obtained. The GPC analyses of copolymers indicated their number averaged chain lengths were in excess of a polystyrene with a molecular weight of 20,000. Since the intrinsic viscosities of the samples were not obtained (small sample size), the exact molecular weights of these samples could not be obtained. The chain lengths were determined in relation to polystyrene standards. Copolymer 18 (see experimental section) exhibited a weight-averaged chain length of 811 Å, for example. A high degree of polymerization was obtained in each case.

The penultimate reactivity ratios were calculated by using the computer programs described elsewhere [13] which employed a nonlinear fitting of the composition-conversion data to the integrated

TABLE 1. Copolymerization of 2,3,4-Trimethyl-3-pentyl Methacrylate (I) with Styrene: Composition-Conversion Data Obtained at 60°C in Benzene Solutions with AIBN Initiators^{a,b}

Expt. no.	Monomer feed (g)		AIBN (g × 10 ⁻⁴)	Phenyl ether (g)	Benzene (g)	I in feed (mole %)	Time (hr)	Conversion to polymer (wt %)	M _i in polymer (mole %)
	I	Styrene							
1	0.1903	0.2333	5	0.1901	1.1803	29.99	16.337	12.61	28.90
2	0.4209	0.0933	6	0.1849	1.1760	70.32	16.337	11.67	60.33
3	0.3060	0.1676	7	0.1882	1.2033	48.95	9.239	7.85	42.64
4	0.5471	0.0396	8	0.1975	1.1727	87.89	9.239	13.36	73.84
5	0.0730	0.3069	6	0.1976	1.1850	11.11	10.108	9.40	13.73
6	0.3621	0.1278	3	0.1914	1.1790	59.81	10.108	6.82	43.94
7	0.2389	0.1975	4	0.1997	1.1784	38.85	10.108	5.93	38.85
8	0.5637	0.0286	3	0.1997	1.1842	91.19	7.594	4.00	77.73
9	0.0479	0.3380	4	0.2034	1.1785	6.93	7.594	6.06	10.84
10	0.1436	0.2500	2	0.1874	1.1730	23.18	10.214	6.33	24.16
11	0.5587	0.0269	4	0.1945	1.1855	91.60	10.214	7.33	78.84
12	0.3660	0.1337	4	0.1940	1.1730	58.98	10.214	7.74	50.65
13	0.0320	0.2459	3	0.2105	1.1820	6.40	10.214	6.69	8.84
14	0.5633	0.0163	4	0.1914	1.1858	94.78	5.000	2.88	85.16
15	0.3646	0.1265	2	0.1833	1.1838	60.22	5.000	2.12	54.16

(continued)

TABLE 1 (continued)

Expt. no.	Monomer feed (g)		AIBN ($g \times 10^{-4}$)	Phenyl ethyl ether (g)	Benzene (g)	I in feed (mole %)	Time (hr)	Conver- sion to polymer (wt %)	M_i in polymer (mole %)
	I	Styrene							
16	0.1519	0.2537	5	0.1987	1.1785	23.92	3.500	2.93	30.38
17	0.0417	0.3322	3	0.1982	1.1740	6.19	3.500	2.67	9.09

^aFrom these experiments the calculated penultimate reactivity ratios are $r_1 = 0.23$, $r_1' = 0.59$, $r_2 = 0.59$, $r_2' = 1.34$.

^bThe optimum feed ratios for the penultimate reactivity ratios calculated in this study are $M_1^0/M_2^0 = 13/87$, $88/12$, $97/3$, and $56/42$.

form of the penultimate equation (9). For copolymerization of I and styrene the values were:

$$r_1 = k_{111}/k_{112} = 0.23$$

$$r_1' = k_{211}/k_{212} = 0.59$$

$$r_2 = k_{222}/k_{221} = 0.59$$

$$r_2' = k_{122}/k_{121} = 1.34$$

These results indicate a measurable penultimate effect was involved in copolymerizations. If r_1 was equal to (or close to) r_1' and r_2 was equal to (or close to) r_2' , then the terminal model would be implicated as the copolymerization mechanism. However, r_1 and r_2 are significantly different from r_1' and r_2' , respectively. Furthermore, r_1' is larger than r_1 .

A comparison of r_1' and r_2 shows that when styrene is the penultimate monomer, both styryl and 2,3,4-trimethyl-3-pentyl methacrylyl radicals have an equal preference (factor of 1.7) to add the opposite monomer. However, when monomer I is the penultimate unit the situation changes. 2,3,4-Trimethyl-3-pentyl methacrylyl radicals now have a greater preference to add styrene (4.4 times faster). Furthermore, styryl radicals no longer prefer to add to I when I is the penultimate unit. Instead, styryl radicals now add 1.3 times faster to styrene than to I. In other words, the penultimate effect of the bulky ester group overwhelms the normal electronic preference of styryl radicals to add to methacrylate I. When I is the penultimate unit, the probability of adding styrene is increased when either styrene or I is the terminal unit. Finally, as expected, the penultimate effect of monomer I is greatest when the terminal unit is also I. This constitutes the best evidence yet available in the literature for the existence of a steric penultimate effect.

From the values of r_1 , r_1' , r_2 , and r_2' summarized above, the optimized experimental feed ratios were calculated as described previously [13]. The optimum feed ratios were $M_1/M_2 = 13/87$, $88/12$, $97/3$, and $56/42$. In the seventeen copolymerizations described in Table 1, it should be noted that a large number of these experiments were fairly close to these optimized values. No other study of penultimate effects has ever taken this factor into account while simultaneously treating the data by using the nonlinear least-squares approach [13, 14]. From the standpoint of experimental design, this set of data represents the most rigorous experimental composition-conversion approach for evaluating the possible existence of a penultimate effect which has yet appeared.

EXPERIMENTAL

General

All solvents were carefully dried and distilled by standard procedures. Methacrylyl chloride and diisopropyl ketone were obtained commercially and vacuum distilled prior to use. Infrared spectra were obtained on a Beckman model IR-33 instrument and NMR spectra on a Hitachi-Perkin Elmer 60 MHz model R20B spectrometer. A Varian Associates gas chromatograph model 3700 was employed for all GLC work, and electronic integration was accomplished by using a Hewlett-Packard recorder integrator model number 3380A.

2,3,4-Trimethyl-3-pentanol

Methyl iodide (99.5 g, 0.70 mole) in ether (50 ml) was added dropwise to magnesium shavings (16.6 g, 0.68 mole) in ether (250 ml) at 0°C with vigorous stirring under nitrogen. Upon completion of the addition, the reaction was refluxed for 1 hr. Then diisopropyl ketone (70 g, 0.55 mole) in ether (50 ml) was added to the methyl Grignard reagent from a dropping funnel at 0°C. Following addition, the reaction was stirred at 20-25°C for 2 hr and then hydrolyzed by the dropwise addition of a 10% aqueous solution of NH₄Cl (70 g, 1.31 mole of NH₄Cl). The ether layer was separated, washed with saturated aqueous NaCl solutions and then water (200 ml). The ether layer was dried (MgSO₄, anhydrous), evaporated, and the resulting oil was vacuum-distilled. The alcohol was obtained (42.7 g at 72°C/44-35 Torr) and redistilled through a 16-cm column packed with glass beads. An impure fraction was collected at 76-95°C/105 Torr and a pure (GLC) fraction was obtained at 95°C/105 Torr. Its IR spectrum (neat on KBr plates) exhibited a strong, broad hydroxyl stretch at 3440 cm⁻¹ and prominent absorptions at 2960, 1470, 1380, 1160, 1120, 1040, 992, 908, and 875 cm⁻¹.

2,3,4-Trimethyl-3-pentyl Methacrylate

To a solution of 2,3,4-trimethyl-3-pentanol (52 g, 0.41 mole) in ether (150 ml) in a 2-liter separatory funnel was added a hexane solution of n-butyllithium (2.4 M, 165 ml, 0.39 mole). The solution was stirred gently during the addition. After standing 3 hr the resulting lithium alkoxide was added to an ether solution (100 ml) of methacrylyl chloride (39 g, 0.37 mole) at 0°C over a 30-min period with magnetic stirring. A yellow slurry formed, and after 2 hr the

reaction mixture was poured on ice and washed twice with saturated aqueous sodium chloride solutions. After drying the organic layer over anhydrous MgSO_4 and rotary evaporation, a 78.1 g yield of crude monomer I was obtained. The crude product was distilled through a 15-cm packed column ($59^\circ\text{C}/0.1$ Torr) with a significant loss of yield due to polymerization. The distilled product was redistilled through the same column in the presence of butylated hydroxytoluene which inhibited thermally induced polymerization. The fraction collected at $63^\circ\text{C}/0.1$ Torr and $76^\circ\text{C}/3$ mm was pure according to GLC analysis, and 17.9 g of I was collected. The IR spectrum (neat on KBr plates) exhibited a strong carbonyl stretch at 1720 cm^{-1} , carbon-carbon double bond stretching at 1637 cm^{-1} , C-O stretching at 1140 and 1180 cm^{-1} , and vinyl hydrogen out-of-plane bending absorptions. NMR (CCl_4) δ 0.95 (d, 12, $J = 10$ Hz, isopropyl methyls), 1.42 (s, 3, CH_3), 1.19 (d of d, 3, $J_{\text{t-allyl}} = 2.2$, $J_{\text{c-allyl}} = 1.6$ Hz, $\alpha\text{-CH}_3$), 2.39 (heptet, 2, $J = 10$ Hz, hydrogens at 2 and 4), 5.33 (m, 1, vinyl hydrogen cis to carbonyl), 5.90 (m, 1, vinyl hydrogen trans to carbonyl).

Copolymerization of 2,3,4-Trimethyl-3-pentyl Methacrylate with Styrene

All polymerizations were conducted in sealed 8-mm glass tubes. In a typical reaction, AIBN, 2,3,4-trimethyl-3-pentyl methacrylate, styrene, phenyl ethyl ether, and benzene were weighed into a weighing flask on an analytical balance. The solution was divided into two samples which were introduced into 8-mm reaction tubes. The tubes were degassed by three consecutive freeze-pump-thaw cycles and sealed under vacuum. One of the two samples was placed, immediately, in a freezer in the dark to serve as a calibration standard. The second tube was placed in a water bath at 60°C . After a specified reaction time calculated to give a low conversion to copolymer (typically 3.5 to 16 hr) the tube was cooled to room temperature and opened for GLC analysis (on $1/8$ in. \times 4 ft, OV-225 (7%) on Chromasorb W, 100/120 mesh, stainless steel column, 80°C , detector 200°C , filament current 175 mA, flow rate $23\text{ cm}^3/\text{min}$ of He). Alternate injections of the calibration standard and the reaction mixture were made and the consumption of monomers was calculated using the phenyl ethyl ether as the internal standard. From 6 to 12 repetitive injections of the reaction solution and calibration standard were made for every reaction to determine a single composition-conversion point. The styrene peak was essentially constant for each reaction but some fluctuations occurred in the peak area of monomer I for these repetitive injections. Thus, an average of all the values was used.

An extra copolymerization was carried out to higher conversion for gel permeation chromatographic (GPC) analysis by using a 60:40 mole ratio of I:styrene as the feed. The GPC of this copolymer (i. e., 18) exhibited a single smooth curve with a molecular size dispersion from 99 to 3900 Å (corresponds to 4,000 to 160,000 molecular weight for polystyrene), a number-averaged chain length of 552 Å (this corresponds to 23,000 molecular weight for polystyrene), and a weight averaged chain length of 811 Å (corresponding to a 33,500 molecular weight for polystyrene).

CONCLUSIONS

The penultimate equation (9) will always fit any set of experimental composition-conversion data better than the terminal copolymer equation. However, penultimate effects will give $r_1' > r_1$. If curve-fitting of random data was involved, then this result would be obtained in only one-half of the cases. Thus, despite the better fit of the penultimate model, a basis for eliminating the terminal model in favor of the penultimate model still exists. When the terminal model operates, the values of r_1 and r_1' , calculated using the penultimate model, should be approximately equal, as should be r_2 and r_2' . Previously, we studied several cases where hypothetical experimental error was introduced into terminal model data [13]. Fitting those data to equation (9) resulted in similar values for r_1 and r_1' and for r_2 and r_2' . The values of the reactivity ratios obtained for the copolymerizations of I and styrene in this work are significantly different and constitute a reasonable case for a steric penultimate effect by monomer I.

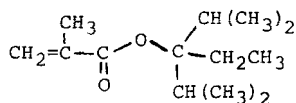
Caution, however, should be applied to these conclusions. In order to establish, definitively, a penultimate effect, accurate experimental data is still required. The use of the optimized, nonlinear, least squares, sequential approach to obtaining penultimate ratios does not remove the need for precise experiments [13]. It was for this reason that the GLC analytical procedure was used in this work. The largest source of error in the method employed here was the reproducibility of the chromatographic results. Each composition-conversion point was established by carefully examining the results from six to twelve injections per data point. The concentration of styrene observed by GLC fluctuated only very slightly for the different injections of any given sample. The concentrations of I exhibited a somewhat larger fluctuation and it is this error that constitutes the largest experimental error encountered in these studies. Apparently, traces of monomer I either hydrolyzed or decomposed on the column. Overall, however, these results are more accurate than

any other published study of the penultimate effect investigated by the composition-conversion approach.

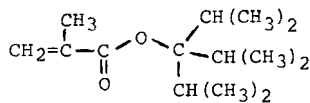
A second caution involves the difference in fit between the models. The sum of squares for the penultimate model was 0.0105 while that for the best terminal fit ($r_1 = 0.266$, $r_2 = 0.653$) was 0.0124. We cannot rigorously exclude the terminal model on the basis of current experiments and it is not possible to calculate true variances for this system.

The use of linear estimation procedures can lead to errors which are often overlooked by the experimenter [18-22]. Our approach guarantees the experimenter the most efficient use of his data and permits an objective probabilistic statement to be made regarding the reliability of his estimates. The experimenter is able to choose his experiments in the most economical way while providing the most information per experiment.

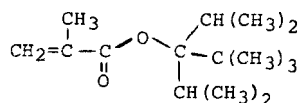
Is there a true steric penultimate effect in the copolymerizations of I and styrene? While the evidence presented here appears reasonable that such an effect has been detected, it must be kept in mind that the penultimate equation (9) will always fit experimental data better than the terminal equation. While r_1' was greater than r_1 and the parameters did make "chemical sense", it would still be safer to wait for substantiating data from a homologous series of related copolymerizations. For example, if the penultimate interpretation of this study is indeed correct, one would predict the penultimate effect could be enhanced by using a monomer, similar to I, with an even more bulky ester group (as long as such a monomer readily homopolymerizes). Three such monomers are II-IV. Monomer II is slightly more bulky than I, since it has a 3-ethyl function in place of the 3-methyl group of I. Monomers III and IV are progressively more bulky because the substituent at the 3 position has been changed to an isopropyl and tert-butyl, respectively. On going from I through IV, one would predict the steric penultimate effect would increase in



II



III



IV

styrene copolymerizations. Thus, the values of r_1 should decrease and r_2' should increase along this series. Establishing such a trend would go a long way toward confirming, definitively, the existence of a steric penultimate effect.

In recent years a large number of studies have claimed the charge-transfer complex model operates in a variety of copolymerizations. Only a few of these studies have attempted a rigorous approach to the problem [23-25]. On the other hand, the penultimate model has not been the subject of much experimental work. In most cases, the amount of monomer charge-transfer complex present under copolymerization conditions is so low that very high orders or reactivity of the complex are required to account for observed results. Thus, the charge-transfer hypothesis could be highly suspect in many cases where it has been invoked. This is especially true in light of opposing arguments that charge-transfer complexation might indeed reduce activity [40]. Therefore, we conclude that the penultimate effect model should continue to be seriously considered and experimentally tested.

REFERENCES

- [1] E. Merz, T. Alfrey, and G. Goldfinger, J. Polym. Sci., **1**, 75 (1946).
- [2] W. G. Barb, J. Polym. Sci., **11**, 117 (1953).
- [3] G. E. Ham, J. Polym. Sci., **14**, 87 (1954).
- [4] G. E. Ham, J. Polym. Sci., **54**, 1 (1961).
- [5] G. E. Ham, J. Polym. Sci., **61**, 9 (1962).
- [6] M. Litt and F. W. Bauer, in Macromolecular Chemistry, Prague 1965 (J. Polym. Sci. C, 16) O. Wichterle and B. Sedláček, Eds., Interscience, New York, 1967, p. 1551.
- [7] K. Ito and Y. Yamashita, J. Polym. Sci. A-1, **4**, 631 (1966).
- [8] M. Berger and I. Kuntz, J. Polym. Sci. A, **2**, 1687 (1964).
- [9] A. D. Ketley, Stereochemistry of Macromolecules, Vol. 3, Dekker, New York, 1968, Chaps. 1, 2.
- [10] K. Bacon, Newer Methods of Polymer Characterization, Interscience, New York, 1964.
- [11] H. J. Harwood and W. M. Ritchey, J. Polym. Sci. B, **2**, 601 (1964).
- [12] H. J. Harwood, in The Computer in Polymer Science (J. Polym. Sci. C, 25), J. B. Kinsinger, Ed., Interscience, New York, 1968, p. 37.
- [13] C. U. Pittman, Jr., and T. D. Rounsefell, J. Polym. Sci. Polym. Chem. Ed., **11**, 621 (1973).
- [14] C. U. Pittman, Jr., and T. D. Rounsefell, in Computers in Chemistry and Instrumentation, Vol. 6, J. S. Mattson, H. B. Mark, Jr., and H. C. MacDonald, Jr., Eds., Marcel Dekker, New York, 1977, Chap. 5.

- [15] C. U. Pittman, Jr., and T. D. Rounsefell, Macromolecules, **8**, 46 (1975).
- [16] D. W. Marquardt, J. Soc. Ind. Appl. Math., **11**, 431 (1963).
- [17] D. W. Marquardt, Chem. Eng. Progr., **55**, 65 (1959).
- [18] D. W. Behnken, J. Polym. Sci. A, **2**, 645 (1964).
- [19] G. E. P. Box and H. L. Lucas, Biometrika, **46**, 77 (1959).
- [20] E. M. L. Beal, J. Roy. Statist. Soc., **B22**, 41 (1960).
- [21] P. W. Tidwell and G. A. Mortimer, J. Polym. Sci. A, **3**, 369 (1965).
- [22] P. W. Tidwell and G. A. Mortimer, J. Macromol. Sci.—Revs. Macromol. Chem., **C4**, 281 (1970).
- [23] J. A. Seiner and M. Litt, Macromolecules, **4**, 308 (1971).
- [24] M. Litt, Macromolecules, **4**, 312 (1971).
- [25] M. Litt and J. A. Seiner, Macromolecules, **4**, 314, 316 (1971).
- [26] T. Otsu, T. Ito, and M. Imoto, in Macromolecular Chemistry, Prague 1965 (J. Polym. Sci., C, **16**), O. Wichterle and B. Sedláček, Eds., Interscience, New York, 1967, p. 2121.
- [27] T. Otsu, T. Ito, and M. Imoto, J. Polym. Sci., A, **2**, 2901 (1964).
- [28] J. C. Bevington and B. W. Malpass, J. Polym. Sci., A, **2**, 1893 (1964).
- [29] J. C. Bevington and B. W. Malpass, Eur. Polym. J., **1**, 19 (1965).
- [30] K. Chikanishi and T. Tsuruta, Makromol. Chem., **73**, 231 (1964).
- [31] G. G. Cameron, D. H. Grant, N. Grassie, J. E. Lamb, and I. C. McNeil, J. Polym. Sci., **36**, 173 (1959).
- [32] G. M. Burnett, P. Evans, and H. W. Melville, Trans. Faraday Soc., **49**, 1096, 1105 (1953).
- [33] J. A. Howell, M. Izu, and K. F. O'Driscoll, J. Polym. Sci. A-1, **8**, 699 (1970).
- [34] M. Izu and K. F. O'Driscoll, Polym. J., **1**, 27 (1970).
- [35] G. G. Lowry, J. Polym. Sci., **42**, 463 (1960).
- [36] J. E. Hazell and K. J. Ivin, Trans. Faraday Soc., **58**, 342 (1962); ibid., **61**, 2330 (1965).
- [37] A. A. Durgaryan, Vysokomol. Soedin., **8**, 790 (1966).
- [38] T. Alfrey and A. V. Tobolsky, J. Polym. Sci., **38**, 269 (1959).
- [39] H. Sawada, J. Polym. Sci. A, **3**, 2483 (1965); J. Polym. Sci. A-1, **5**, 1383 (1967).
- [40] A. Ledwith, Polym. Preprints, **17**(2), 614 (1976).

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