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### Copolymerization of 2-Ethyl Hexyl Acrylate with Styrene in the Presence of $ZnCl_2$

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## **COPOLYMERIZATION OF 2-ETHYL HEXYL ACRYLATE WITH STYRENE IN THE PRESENCE OF $ZnCl_2$**

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### **ABSTRACT**

A copolymer of 2-ethyl hexyl acrylate–styrene was prepared in the presence of  $ZnCl_2$ . The formation was studied by infrared spectroscopy. A study of the final copolymer as a function of the initial monomer composition as well as observation of the variation in intensity of the carbonyl peak from UV spectra confirmed the presence of an alternating copolymer. Solubility trials showed that no homopolymer was formed. The copolymer was characterized by IR, NMR, and solubility tests. It is suggested that the polymerization proceeds through a two-step polymerization mechanism: by coordination followed by polymerization on the alternating copolymer of the chain ends of the residual styrene. The reactivity ratios of the comonomers were determined and found to be 0.3 and 0.04 for the 2-ethyl hexyl acrylate/styrene system.

## INTRODUCTION

In an earlier paper [1] dealing with the copolymerization of butyl acrylate with styrene in the presence of  $ZnCl_2$ , we found styrene blocks in the alternating copolymer. This finding is in contrast to that of the methyl methacrylate-styrene system [2] where the alternating copolymer was mixed with styrene homopolymer. The fact that no homopolymer was found in the former case indicates that the polymerization proceeds by a two-step mechanism and that the size of the styrene blocks is a function of the stoichiometric excess of styrene.

The formation of a complex with  $ZnCl_2$ , as in the methyl methacrylate case, is a critical and essential step required before the actual polymerization occurs. These polymerizations were conducted successfully in both the presence [3] and the absence of water, although the presence of water somewhat affected the yield. Other workers used either organic solvents [4-20] or no solvents [21, 22]. They used initiators, such as AIBN [17], and most of their work was done with methacrylates [23, 24].

The present paper reports, for the first time, the preparation of an alternating copolymer of 2-ethyl hexyl acrylate-styrene in the presence of  $ZnCl_2$ . This copolymer contains long sequences of styrene at its ends. The reaction was carried out in both the presence and the absence of water. No initiator or activator was used in the reaction. The effects of the monomers ratios and of the  $ZnCl_2$  were studied, and the reactivity ratios were determined [25, 26].

## EXPERIMENTAL

### Material

The styrene used was supplied by Aldrich Chemical Co., and the 2-ethyl hexyl acrylate (2-EHA) was obtained from Merck Chemical Co. All the monomers were washed with a 10% NaOH aqueous solution and then with distilled water until a neutral pH was reached. The styrene was dried over calcium chloride, the 2-EHA was dried over anhydrous sodium sulfate, and then the monomers were distilled. The  $ZnCl_2$ , also obtained from Merck Chemical Co., was used as received.

### Copolymerization Procedure

The copolymerization of 2-ethyl hexyl acrylate with styrene in the presence of  $ZnCl_2$  was conducted under the same conditions as described previously [1]. In the absence of water, a white mass appeared after 45 minutes of polymerization; it took 1.5 hours for the mass to appear when water was present. The solid mass obtained was purified according to a method described elsewhere [1], except for the drying which was done at 60°C and under vacuum.

Seven polymerizations were conducted, some were interrupted after 10, 15, or 40 minutes of reaction. The recipes of these polymerizations are given in Table 1. After each polymerization the residual liquid was analyzed for its monomer content by optical density. The polymer obtained after purification and drying was analyzed by the same technique.

TABLE 1. Effect of the Concentration of the Reactants on the Yield and on the Carbonyl Absorption Band of the 2-EHA/Styrene Copolymer

Experiment	2-EHA, moles	Styrene, moles	ZnCl <sub>2</sub> , moles	Reaction time, minutes	Yield, wt%	Absorption band intensity, 280 m $\mu$
1	0.1	0.9	0.1	10	16.9	0.64
2	0.2	0.8	0.2	10	11.6	0.70
3	0.3	0.7	0.3	10	3.6	0.70
4	0.5	0.5	0.5	10	1.5	0.80
5	0.7	0.3	0.7	15	1.7	0.61
6	0.8	0.2	0.8	40	2.2	0.52
7	0.9	0.1	0.9	40	1.7	0.44

### Purification of the Polymers

The copolymers were separated from the homopolymers by selective solubilization. Two solvents were used: cyclohexane and isobutanol. The solubility parameters of these solvents are 8.2 and 10.5, respectively [27]. The acrylate homopolymer (at room temperature) as well as the polystyrene (below 35°C) are both insoluble in cyclohexane whereas the copolymer is soluble and stays solubilized even at 0°C [28]. This technique permitted the extraction of the copolymer.

The homopolymer of 2-ethyl hexyl acrylate is soluble in isobutanol whereas its copolymer with styrene is not. Solubility tests were performed with isobutanol. Even after boiling in isobutanol, no homopolymer was found in the solution.

## RESULTS

### Preparation of the 2-Ethyl Hexyl Acrylate–Styrene Copolymer

The mixing of the 2-ethyl hexyl acrylate in a 1:1 molar ratio with ZnCl<sub>2</sub> at –20°C for 20 minutes gave a homogeneous solution. The presence of a complex was confirmed by IR analysis. The method has been described elsewhere [1].

Copolymerization of this complex with styrene was conducted under agitation for 45 minutes. A white solid mass was formed. The entire system was then held without agitation for 4 hours in order that the reaction might proceed. The polymer was purified. The final product was a white viscous mass with a 73 wt% reaction yield. It was soluble in CHCl<sub>3</sub>, toluene, ethyl acetate, and methylene chloride. These solubility results indicate no homopolymer is present. IR and NMR analyses were also run on these polymers, and they confirmed the presence of a copolymer.

### Effect of Water on the Copolymerization

When water was added to the reacting medium, it lowered the yield to 65 wt% (Table 2). This was not totally unexpected, and confirmed the results of other workers [29].

TABLE 2. Effect of Water on the Conversion of the Monomers

Styrene, moles	2-EHA, moles	ZnCl <sub>2</sub> , moles	H <sub>2</sub> O, moles	Reaction yield, %
1.0	1.0	1.0	0	73.0
1.0	0.8	0.8	0	74.5
1.0	0.8	0.8	0.5	65.0

### Reaction Yield and Composition of the Copolymer

As before, in order to determine the presence of an alternating copolymer in the copolymerization of 2-EHA/styrene, samples of the 2-EHA/styrene copolymer were prepared with different monomer and ZnCl<sub>2</sub> ratios. The experiments were carried out at 50°C for 10, 15, and 40 minutes under a nitrogen blanket. The samples were characterized by UV, and the reaction yield was calculated (Table 1).

### Determination of the Reactivity Ratios

The reactivity ratios were determined by using the simplified Fineman-Ross equation [25] with  $f_1$  as the mole fraction of 2-EHA in the monomer mixture,  $f_2$  as the mole fraction of styrene and  $F_1$  the "instantaneous" copolymer composition expressed as mole fraction of 2-EHA. The experimental  $F_1$  and  $f_1$  values are given in Table 3, and the reactivity ratios were found to be 0.3 and 0.04, respectively, for  $r_1$  and  $r_2$ . Another way of obtaining the  $r_1$  and  $r_2$  values is by solving the copolymer equation [30] for one of the reactivity ratios, for each given feed composition corresponds to a straight line for a plot of  $r_1$  vs  $r_2$  [26]:

$$r_2 = \frac{[M_1]}{[M_2]} \left[ \frac{d[M_2]}{d[M_1]} \left( 1 + \frac{[M_1]}{[M_2]} r_1 \right) - 1 \right] \quad (1)$$

where  $[M_1]$  and  $[M_2]$  are the molar concentrations of the monomers 1 and 2, respectively, in the reaction medium.

Normally these lines should intersect at one point to give  $r_1$  and  $r_2$ . Experimentally, however, they do not.

TABLE 3.  $F_1$  and  $f_1$  Values for the 2-EHA/Styrene System

$F_1$	$f_1$
0.46	0.10
0.50	0.20
0.50	0.30
0.57	0.50
0.44	0.70
0.37	0.80
0.31	0.90

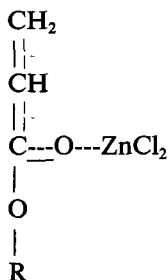
## DISCUSSION

## Formation of a Ternary Complex

In order to confirm the formation of a complex of the styrene-acrylate-ZnCl<sub>2</sub> type, infrared spectra of the acrylate monomers were taken. The following spectra were taken: 2-EHA, an equimolar mixture of 2-EHA and ZnCl<sub>2</sub>, and finally a mixture of 2-EHA-ZnCl<sub>2</sub>-styrene at -20°C which was heated to 40°C. The results are given in Table 4.

The formation of a complex may be identified by noting the change in the frequency of the C=O absorption band from 1720 to 1590 cm<sup>-1</sup> which occurs after a few minutes at 40°C. This result suggests a mechanism similar to that for the addition of ZnCl<sub>2</sub> at low temperature to the acrylate, followed by the addition of styrene. Under these conditions a ternary complex St-2-EHA-ZnCl<sub>2</sub> is formed which changes the broad absorption band to a narrow band without moving its position, i.e., 1720 cm<sup>-1</sup>. The same phenomena occurs when butyl acrylate is reacted with styrene in the presence of ZnCl<sub>2</sub> [1].

The 2-EHA monomer forms a complex with ZnCl<sub>2</sub> as evidenced by a shift in the C=O band frequency.



Also note the existence of three relatively intense peaks in the 1950-1800 cm<sup>-1</sup> area for the complexed material (Fig. 1). We attribute these peaks to substituted alkyl groups or to the complexed 2-EHA with styrene in the polymer chain. This is confirmed by the absorption bands at 3600 and 3450 cm<sup>-1</sup> which are due to the intermolecular dimeric or polymeric association which disappears in the purified material (Fig. 2). The presence of substituted alkyl groups is indicated in the NMR spectra shown in Fig. 3.

## Determination of the Degree of Alternation in the Copolymer

The UV results given in Table 2 were obtained from a 0.5% w/v sample of the polymers with chloroform as the solvent. These results were obtained after 10

TABLE 4. Effect of ZnCl<sub>2</sub> on the IR Carbonyl C=O and C=C Bands

	C=O, $\nu$ , cm <sup>-1</sup>	$\Delta\nu$ , cm <sup>-1</sup>	C=C, $\nu$ , cm <sup>-1</sup>	CH <sub>3</sub> , CH <sub>2</sub> , $\nu$ , cm <sup>-1</sup>
2-EHA	1720	—	1620	2900-2800
2-EHA-ZnCl <sub>2</sub>	1720-1590	-130	1590	2900-2800
2-EHA-ZnCl <sub>2</sub> -styrene (low temperature)	1720	—	1600	2900-2800

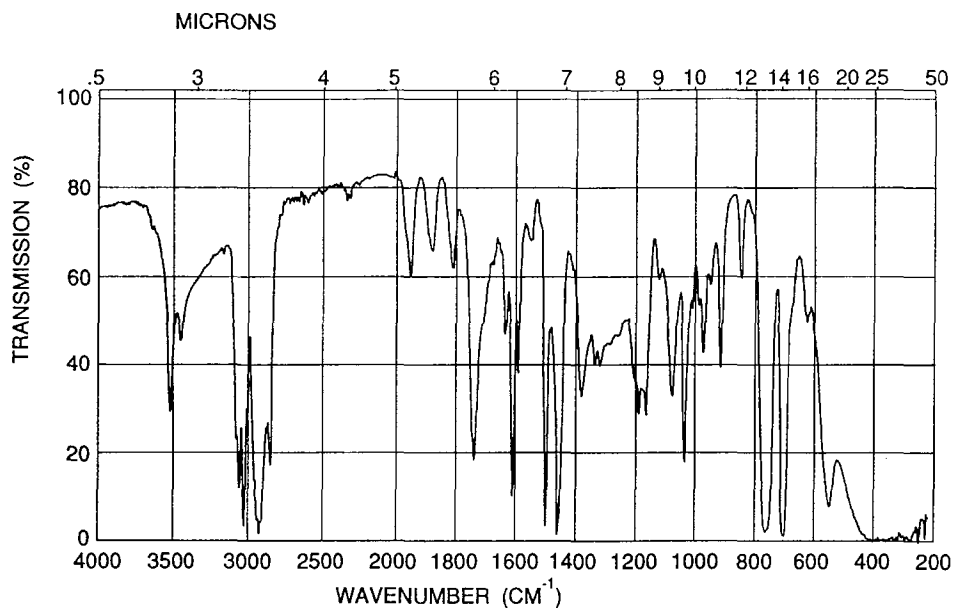


FIG. 1. Infrared spectra of a complexed 2-ethyl hexyl acrylate-styrene copolymer.

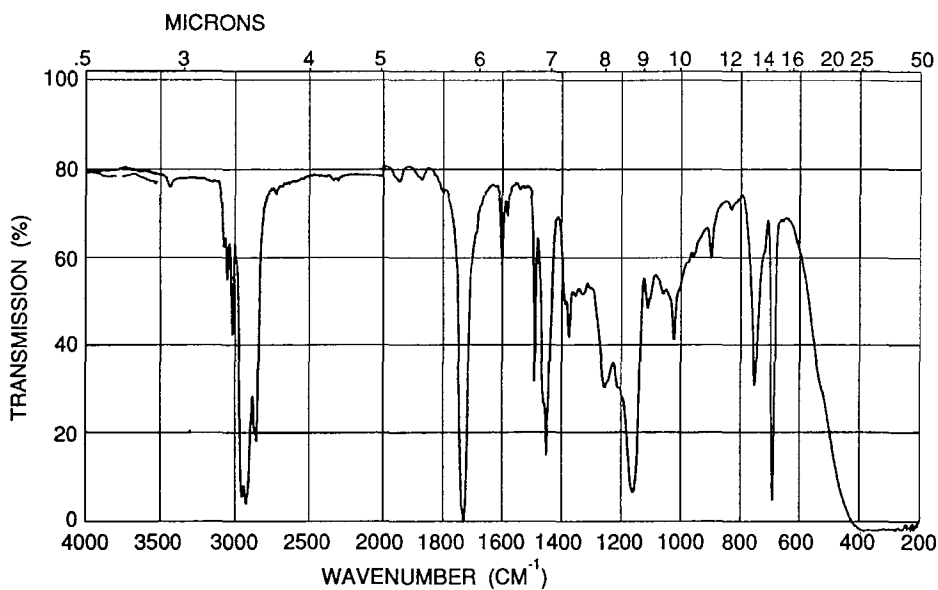


FIG. 2. Infrared spectra of an alternating purified 2-ethyl hexyl acrylate-styrene copolymer.

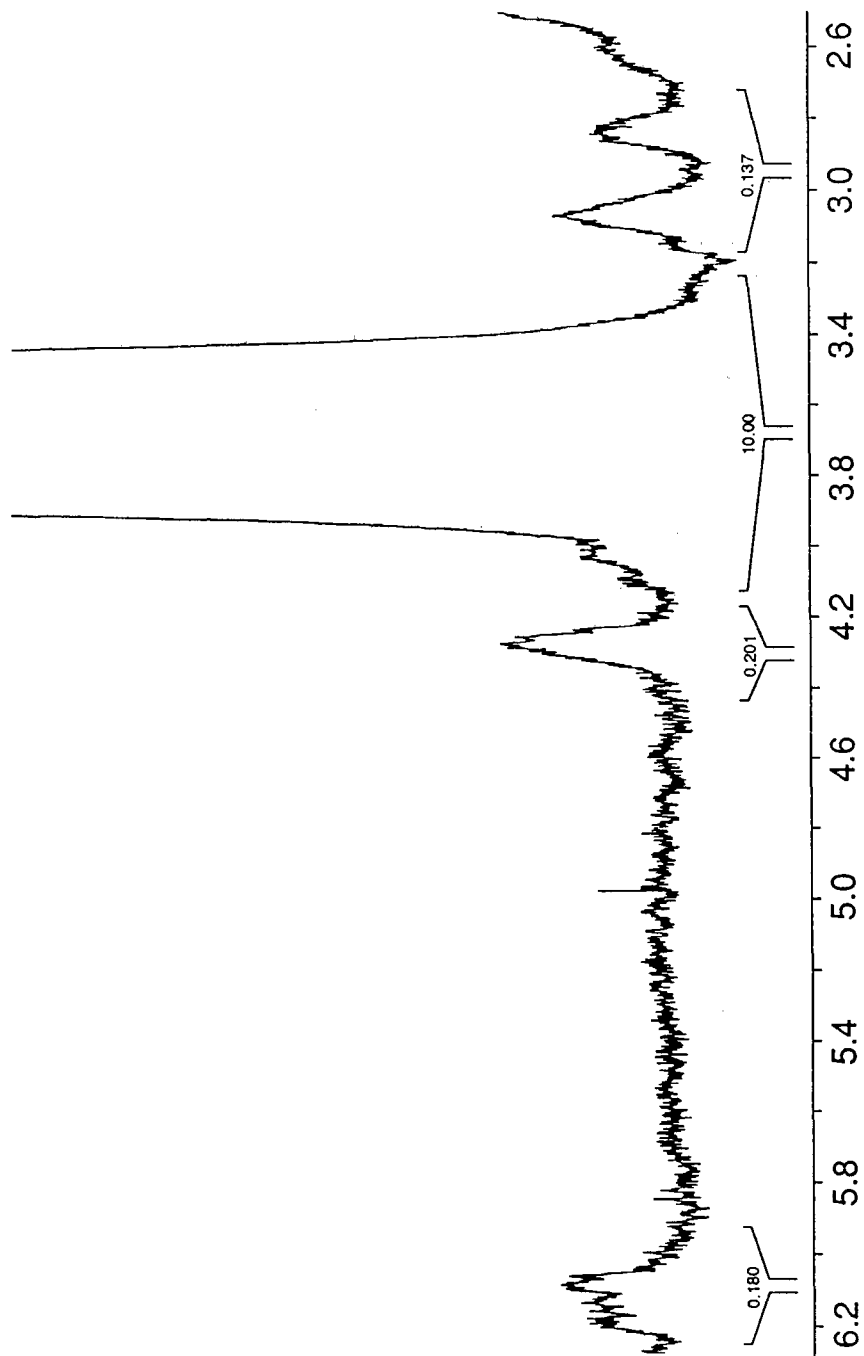


FIG. 3. <sup>1</sup>H spectrum (400.13 MHz) of the styrene-2-EHA copolymer.



minutes of reaction and put into the form of a graph (Fig. 4). The UV measurements were taken after 10, 15, and 40 minutes of reaction. Ten minutes was selected as our standard reference reaction time. As the intensity of the carbonyl peak is a function of the quantity of acrylate in the copolymer, it was used to monitor the composition of the copolymer. Note that a plateau occurs in an area overlapping a 0.2–0.3 mole fraction of 2-EHA in the monomer feed when the mole fraction of 2-EHA in the copolymer is 0.5 (Fig. 5).

Note also in Fig. 4 the plateau overlapping the 2-EHA composition of 0.15 and 0.30 mole fractions; this suggests the presence of a 50/50 alternating copolymer of 2-EHA and styrene. The polymerization might proceed through a mechanism similar to the one suggested for methyl methacrylate and styrene [3] as far as alternating copolymer formation is considered.

The large decrease of the absorption band intensity of the carbonyl group of 0.52 and 0.44 with higher 2-EHA mole fractions of 0.8 and 0.9, respectively, and the solubility trials indicate that there is no homopolymer present and that a nonalternating structure is present as either a nonequimolar block or as a long sequence of nonequimolar units.

This suggestion is suggested by the following experimental results. In Fig. 6 the reaction yield after 10 minutes of reaction is plotted against the mole fraction of styrene in the initial monomer mixture when the 2-EHA/ $ZnCl_2$  ratio is kept constant and equimolar. Note that there is an exponential increase in the yield up to 16.9%

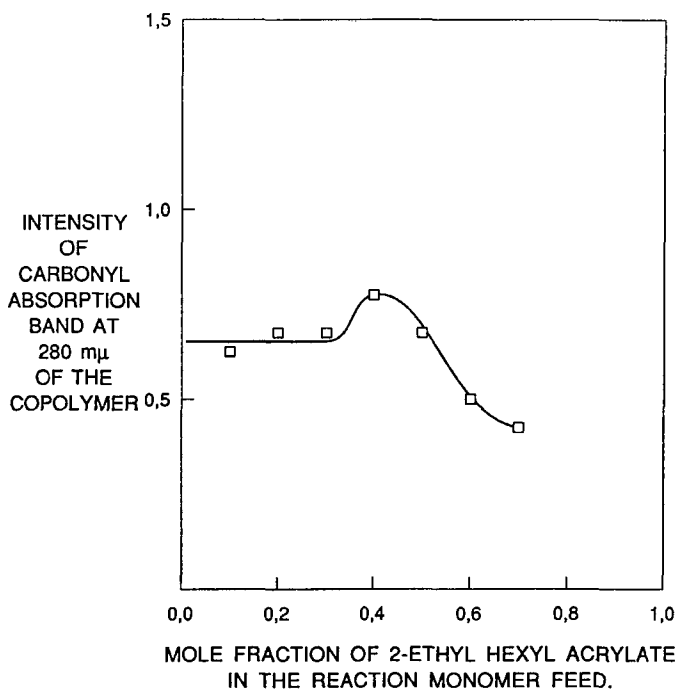


FIG. 4. Intensity of carbonyl absorption band at 280 mμ of the copolymer vs mole fraction of 2-EHA in the reaction feed after 10 minutes of reaction.

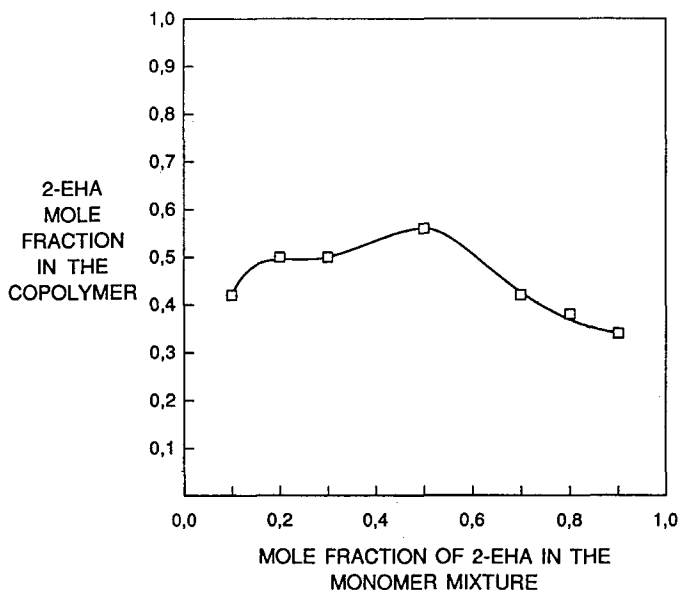


FIG. 5. Mole fraction of 2-EHA in the copolymer vs mole fraction of 2-EHA in the monomer mixture.

conversion after 10 minutes of polymerization for mole fractions of 0.1, 0.1, and 0.9 of 2-EHA,  $ZnCl_2$ , and styrene, respectively.

The copolymerization with a molar ratio of 1/1/1 for styrene, 2-EHA, and  $ZnCl_2$  yielded 70% monomer conversion after 45 minutes of reaction whereas such a

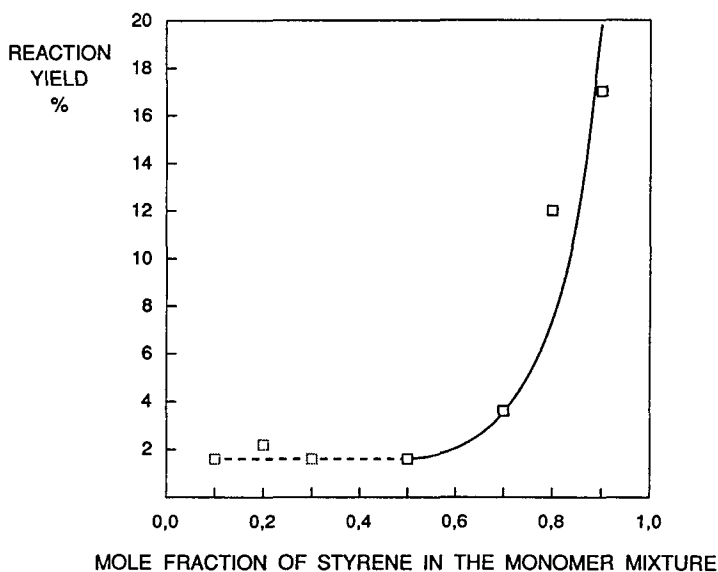


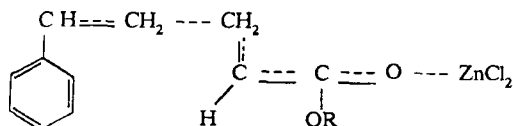
FIG. 6. Reaction yield vs initial concentration of styrene.

conversion was never obtained in the absence of  $ZnCl_2$  and in the presence or absence of a radical initiator. This suggests that the reaction does not proceed by a normal radical mechanism, but rather by a coordination-type mechanism.

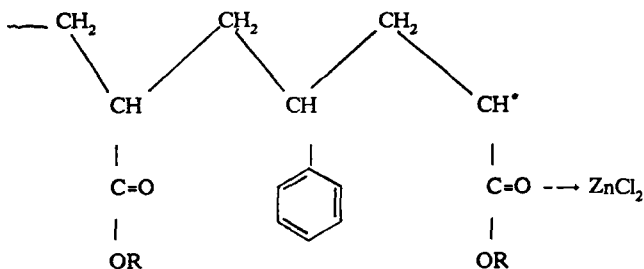
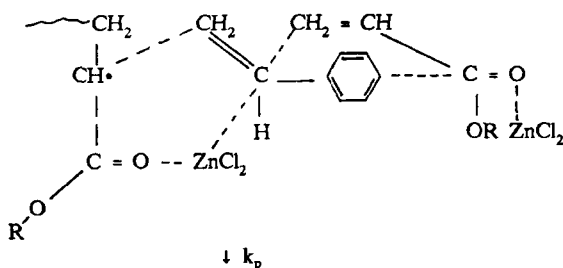
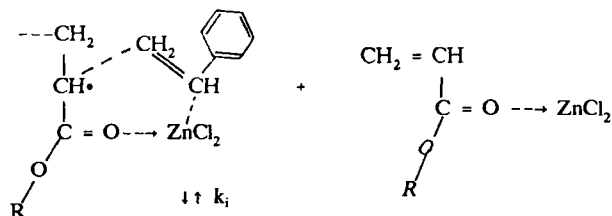
The reaction yield decreases when the concentration of  $ZnCl_2$  or 2-EHA is increased (Table 1). The same phenomenon was noted with butyl acrylate [1] when it was used instead of 2-EHA. In this particular case, a 98% conversion was achieved in spite of nonstoichiometric concentrations of the reactants. This suggests that the mechanism is not entirely a homopolymerization of a ternary complex formed of St-2-EHA- $ZnCl_2$ .

The concentration of styrene affects the reaction yield. For example, with a molar concentration of less than 0.3, the conversion is about 2% and rises with an increasing level of styrene.

In the case of an alternating copolymer, the following mechanisms were suggested. The formation of a complex [31] such as



or the formation of a complexed radical [6]:



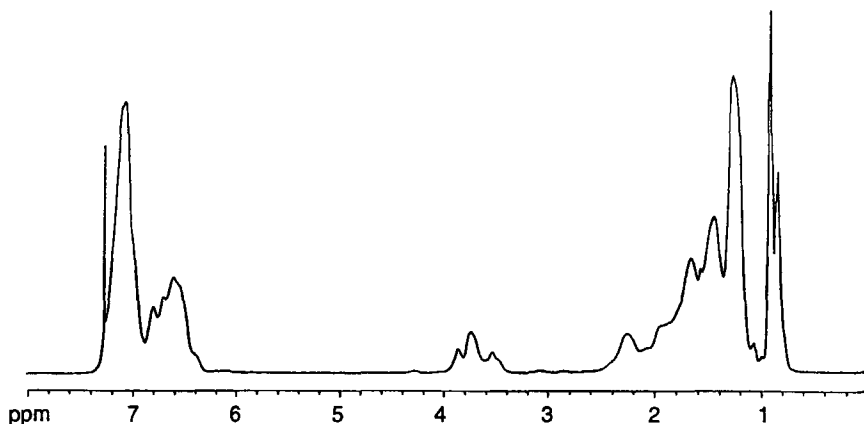


FIG. 7. <sup>1</sup>H spectrum (400.13 MHz) of the 2-EHA-styrene copolymer after 1.5 hours of reaction.

where  $k_i$  and  $k_p$  are the initiation and propagation constants, respectively. Which-ever case is chosen, it does not explain the presence of longer sequences of styrene in the chain.

In Fig. 4, where the initial monomer concentration is plotted against the carbonyl absorption band intensity, note that there is an alternating copolymer for 2-EHA concentrations of 0.15 to 0.55 moles. When the concentration of 2-EHA is increased, the intensity of the absorption band decreases, which is contrary to the butyl acrylate case in spite of the equimolar molar presence of  $ZnCl_2$  with 2-EHA.

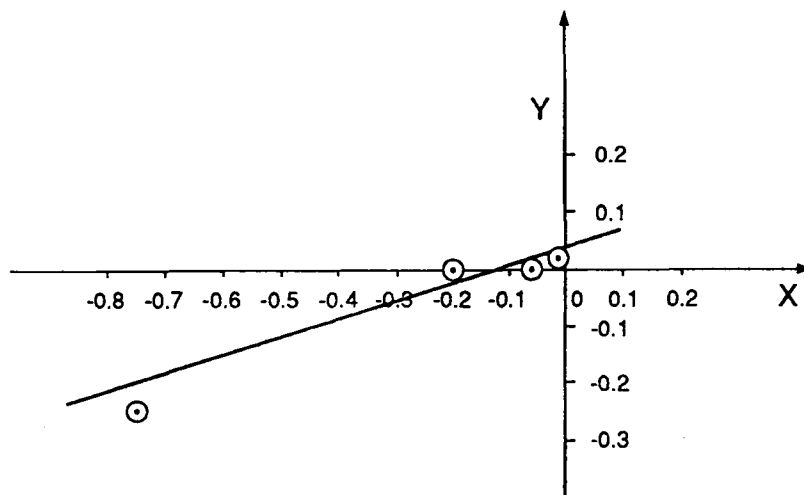


FIG. 8. Determination of reactivity ratios:

$$Y = f_1(1 - 2F_1)/[(1 - f_1)F_1] \text{ and } X = f_1^2(F_1 - 1)/[(1 - f_1)^2F_1]$$

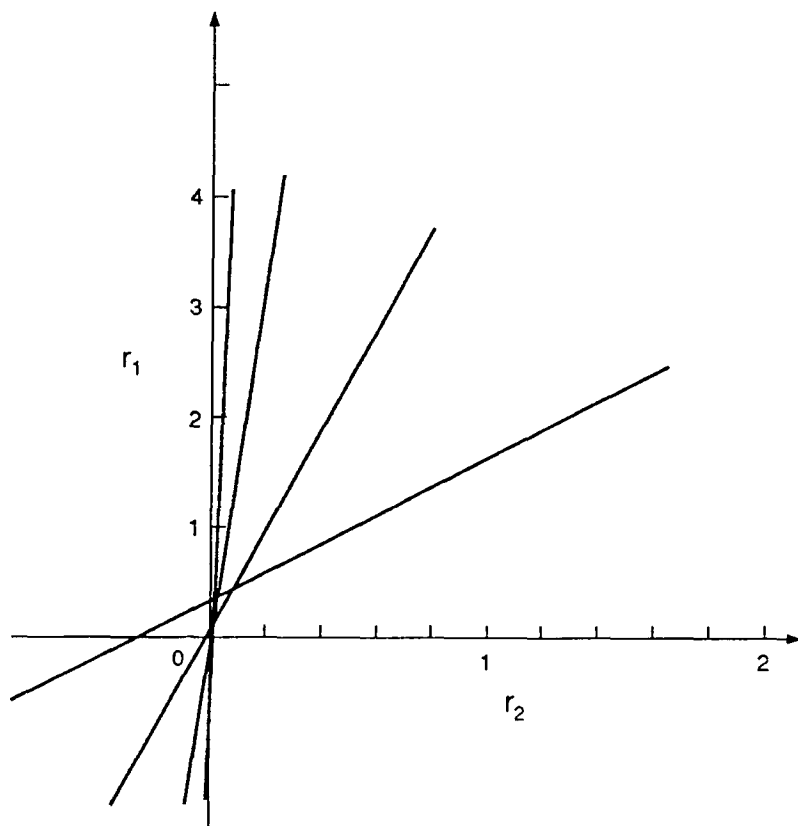


FIG. 9. Reactivity ratio of 2-EHA ( $r_1$ ) vs reactivity ratio of styrene ( $r_2$ ).

No polystyrene homopolymer was present in the butyl acrylate case. This suggests that the copolymer could be a variable structure made up of alternating components combined with styrene units at the chain end or by an alternating part combined with nonequimolar parts.

These hypotheses are confirmed by the results based on the mole fraction of 2-EHA in the initial monomer mixture (Fig. 4). The results are confirmed by NMR spectra when 2-EHA was copolymerized with styrene in the presence of  $ZnCl_2$  with mole ratios of 0.8, 1, and 0.8 (Fig. 7). After 30 minutes of reaction, the composition of the polymer was estimated from the NMR trace to be about 55% 2-EHA. This suggests that for each mole of 2-EHA there is a mole of styrene in the copolymer, as in an alternating copolymer. However, when the polymerization time was 90 minutes, the 2-EHA content changed to 24%, suggesting there was now 1 mole of 2-EHA for each 3.3 moles of styrene.

The reactivity values of the system were determined according to the two methods described previously: the Fineman-Ross equation (Fig. 8) and another method (Fig. 9). Both methods gave the same values for  $r_1$  and  $r_2$ . The reactivity ratio of 2-EHA was found to be 0.3 and the reactivity ratio of styrene was found to

be 0.04. The  $r_1 \times r_2$  value was 0.012, confirming the existence of an alternating copolymer.

## CONCLUSION

It has been shown that when 2-ethyl hexyl acrylate is mixed at  $-20^\circ\text{C}$  with  $\text{ZnCl}_2$ , a complex is formed. This complex reacts with styrene by a coordination mechanism to give an alternating polymer with sequences of styrene groups.

Solubility studies indicate that there is no homopolymer present in the end product. However, as the level of styrene is increased, the copolymer conversion yield is increased. This suggests that the polymerization proceeds by a two-step mechanism. First, an alternating copolymer is formed, followed by the addition of a block styrene polymer on the same polymer chain. In other words, the final polymer is an alternate copolymer with a polymer part constituted essentially of styrene. The polymerizations may be conducted in the presence of water, but that decreases the final conversion. The reactivity ratios for the 2-EHA and styrene system were found to be 0.3 and 0.04.

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