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Copolymerization of butyl acrylate with styrene in presence of $ZnCl_2$

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Summary

Copolymers of butyl acrylate-styrene were prepared in presence of $ZnCl_2$. The formation of a complex was determined by infrared spectroscopy. The copolymers were characterized by IR, NMR and by solubility. The study of their structure as a function of the initial monomer composition and the analysis of UV spectra showing varying intensity of the carbonyl peaks confirmed the presence of an alternating copolymer. The reactivity ratios of the two monomers were determined and found to be 0.1 for both butyl acrylate and styrene.

Introduction

The preparation of alternate copolymers, particularly those of methacrylates, has been reported by many workers[1-19]. The reaction is usually conducted either in solution or in bulk in presence of halide derivative. Most used toluene[3-7, 10-13] dimethyl formamide[14], ethyl acetate[2] or dichloro ethane[16] as diluents while others polymerized in absence of diluent altogether[8,9]. Earlier, azobisisobutyronitrile or benzoyl peroxyde[16] were used as well as photo catalysis. These initiation systems were used in conjunction with a Lewis acid complexing agent, such as $ZnCl_2$[1], $AlCl_3$[7], $SnCl_4$[10], Al $(C_2H_5)_2$ Cl[18], BCl_3[17].

It was noted by that in certain cases a catalyst is not required as the complexing agent is playing this role[15].

Various aspects of this copolymerization have been discussed and it was suggested that it is neither radical nor ionic but proceeds through a complex mechanism[20]. Also we have shown earlier that the reaction can take place in the presence of water[21].

Very little work has been published on the alternating copolymerization of acrylates. We can mention the work by Valuyev et al.[9] with butyl acrylate, Majumdar et al.[22] with methyl fluoroacrylate and Nigam et al.[23] with methyl acrylate.

This paper reports on the preparation of the alternate copolymers of butyl acrylate-styrene in presence of zinc chloride. The reaction was carried out both in presence and absence of water. No catalyst or activator was used. The effects of the butyl acrylate/styrene ratio's and of the concentration of zinc chloride were studied and the reactivity ratios determined.

Experimental

Material

The styrene used was supplied by Aldrich Chemical Co., the butyl acrylate was obtained from Merck Chemical Co. All the monomers were washed with a 10% NaOH aqueous solution and then with distilled water to neutral pH. Finally, the styrene was dried over calcium chloride and the butyl acrylate dried over anhydrous sodium sulfate.

The zinc chloride, also obtained from Merck Chemical Co., was used as received.

Copolymerization Procedure

A. Butyl Acrylate/Styrene Copolymer

The acrylate monomer and zinc chloride were mixed in a molar ratio of 1/1, in a 500 ml reactor using a magnetic agitator. The mixing is done at -20°C until the solution is homogeneous after which it is transfered, under nitrogen atmosphere, to the copolymerization reactor. The styrene is then added to the acrylate-zinc chloride complex solution. The reactor is brought quickly to 50°C using a thermoregulated water bath. The reaction is carried out for one hour under constant agitation. The white precipitate obtained is dissolved in $CHCl_3$ and to this solution a 3% HCl methanol solution is added in a 1/3 ratio. The precipitate is washed with methanol and dried under vacuum at 70°C.

When the polymerization is conducted in presence of water, it is added to the zinc chloride complex solution with the styrene. After 1 1/2 hours the reaction medium is an homogeneous whitish solution.

For the other copolymerizations the operating conditions were held constant except for the reaction time which was lowered in certain cases to 6 min. instead of the usual 1h in order to study the evolution of reaction, at a constant time. The level of butyl acrylate in the reacting medium as well as in the copolymer was determined by optical density of the C=O UV spectra peak.

B. Purification of the Polymers

The copolymers were separated from the homopolymers by selective solubilisation. Two solvents were used: cyclohexane and isobutanol. The acrylate homopolymer at room temperature as well as the polystyrene above 35°C are both insoluble in cyclohexane. The copolymer however was extracted and did not precipitate even at 0°C.

The homopolymer of butyl acrylate is soluble in isobutanol contrary to its copolymer with styrene. Solubility test were performed with isobutanol and even after boiling in isobutanol no homopolymer was found in the solution.

Results

A. Preparation of the Butyl Acrylate-Styrene Copolymer

As shown earlier the first step is the formation of the complex of butyl acrylate/Zinc Chloride. Its presence was confirmed by IR analysis. After one hour of reaction between the complex and the styrene, the solid mass formed blocks the agitator. The reaction medium is however maintained without agitation for 10 hours.

After purification, gravimetric analysis indicated a 98% conversion. The copolymer formed has a melting point of 120°C and is soluble in the following solvents: ethyl acetate, toluene, cyclohexane and chloroform.

The copolymer obtained was analyzed by IR and by NMR.

Effect of water on the copolymerisation.

The copolymerization reaction was performed through the coordination process in presence of water. The operating procedures were similar to the previous ones. In this case the respective molar ratios for the butyl acrylate/styrene/zinc chloride were equal to 0.8, 1.0 and 0.8 respectively with a slight excess of styrene. The water added was equivalent to 5/8 moles of zinc chloride. The presence of water, as shown in table 1, affects negatively the reaction yield. From a 98% reaction yield it drops to 93% and then to 45% when the water is 6 times the level of the $ZnCl_2$ concentration.

TABLE 1
Effect of water on the conversion

Yield %	H_2O moles	$ZnCl_2$ moles	Styrene moles	Butyl Acrylate moles
98	0	0.8	1.0	0.8
93	0.5	0.8	1.0	1.0
45	5.0	0.8	1.0	0.8

Reaction yield and level of butyl acrylate in the copolymer

For the determination of the alternating copolymer in the butyl acrylate/styrene copolymer, copolymers were prepared with different ratios of monomers and $ZnCl_2$. The other parameters were maintained constant only the mixing time was changed to 6mm.

The reaction yield was determined by gravimetry and the level of absorption of the carbonyl group in the copolymer was obtained by UV spectoscopy at 280 millimicrons. The results are given in Table 2.

Table 2

Effect of the concentration of the reactants on the yield and on the intensity of carbonyl absorption band of the butyl acrylate/styrene copolymer.

REACTION	BUTYL ACRYLATE MOLES	STYRENE MOLES	$ZnCl_2$ MOLES	YIELD %	ABSOR.BAND INTENSITY 280 mu
1	0.1	0.9	0.1	26.39	0.52
2	0.2	0.8	0.2	8.27	0.58
3	0.3	0.7	0.3	7.80	0.82
4	0.5	0.5	0.5	3.04	0.84
5	0.7	0.3	0.7	2.23	0.85
6	0.8	0.2	0.8	1.65	0.93
7	0.9	0.1	0.9	1.55	1.54

Determination of the reactivity ratios: r_1 and r_2

The reactivity ratios were obtained by using the simplified Finneman and Ross copolymer composition equation[24] with the monomers composition in the reacting medium and in the copolymer.

The method of intersections was used[25] with f1, the mole fraction of the butyl acrylate in the monomer mixture, and F1, the butyl acrylate level in the copolymer. The f1 and F1 values used are given in Table 3.

Table 3

F1 and f1 values for the butyl acrylate/styrene system.

F1	f1
0.32	0.10
0.36	0.20
0.51	0.30
0.52	0.50
0.54	0.70
0.59	0.80
0.96	0.90

By both methods $r_1=r_2=0.1$, r_1 and r_2 being respectively the reactivity ratios of butyl acrylate and of styrene.

Results and Discussion

Formation of a ternary complex

In order to confirm the formation of a complex of the styrene - acrylate-$ZnCl_2$ type, infra-red spectra were taken of the acrylate monomer, the complexed acrylate monomer with zinc chloride at a 1/1 ratio and the complexed acrylate monomer with zinc chloride to which styrene was added. The results are given in table 4.

The formation of a complex may be noted by the measure of the displacement of the frequency of the large absorption band of C=O from 1720 to 1590 cm-1. This indicates that there is a lowering of the energy of vibration.

After a few minutes at 40°C, a shift in the carbonyl absorption band is observed suggesting that a reaction is proceeding. One may interpret this as the formation of a ternary complex St---BuA---$ZnCl_2$. This modifies the large absorption band in to a sharp one but at its original wave numbers of 1720 cm-1 for the carbonyl group.

Table 4

Effect of $ZnCl_2$ on the I.R. carbonyl C=O band.

	C=O ν (cm-1)	$\Delta\nu$ cm-1	C=C ν cm-1	CH3, CH2 ν cm-1
Butyl Acrylate	1720	---	1620	2900-2800
Bytyl Acrylate-ZnCl2	1590-1720	-130	1590	2900-2800
Butyl Acrylate-ZnCl2-Styrene(low temperature)	1720	0	1600	2900-2800

The same phenomena occurs with the C=C bond. In this case the frequency, originally at 1620 cm-1, goes to 1590 cm-1 to return to 1600 cm-1. A superposition of the spectra of Butyl Acrylate (1), Butyl Acrylate - $ZnCl_2$ (2) and Butyl Acrylate - $ZnCl_2$ - Styrene (3) is given in fig. 1.

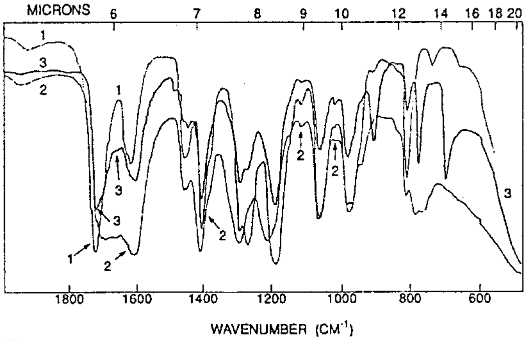


Fig. 1
Infrared Spectras at -20°C

Butyl acrylate (1)
Butyl acrylate - $ZnCl_2$ (2)
Butyl acrylate - $ZnCl_2$ - Styrene (3)

The Butyl Acrylate forms a complex with $ZnCl_2$ as evidenced by a shift in the C=O band frequency.

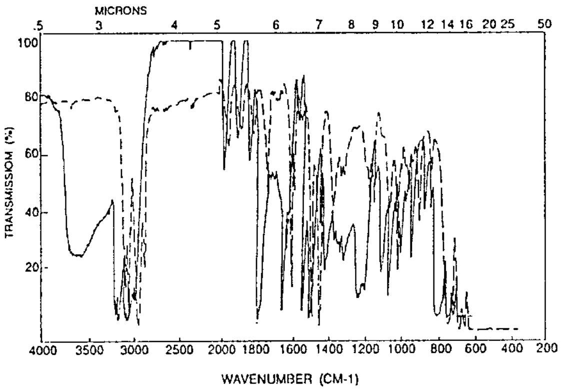


Fig. 2
Infrared Spectra of the Copolymer of Butyl Acrylate - Styrene
Complexed Copolymer ______
Purified Copolymer - - - - -

In fig.2, we have, after 1 1/2 hours of reaction between the Styrene and the Butyl acrylate - $ZnCl_2$ complex, a displacement of the carbonyl group from 1680 cm^{-1} in the complexed material to 1730 cm^{-1} for the purified material. Also to be noted is the existence of three peaks in the 1840 - 2000 cm^{-1} area for the complexed material which are shifted to the 1800-1950 cm^{-1} area. We attribute this to the substituted alkyl groups.

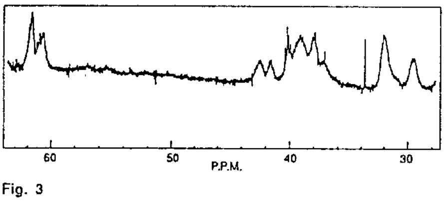


Fig. 3

^1H Spectrum (400,13 MHz) of the Styrene - Butyl acrylate copolymer

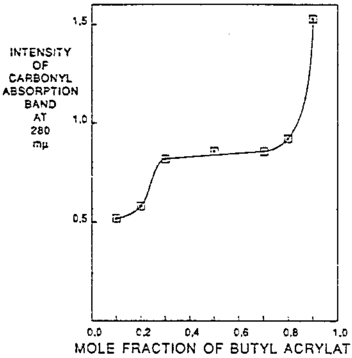


FIG. 4
INTENSITY OF CARBONYL ABSORPTION BAND AT 280 mµ vs MOLE FRACTION OF BUTYL ACRYLATE IN THE MONOMER FEED.

The subtituted alkyl groups are furthermore indicated by the NMR spectra, see fig. 3. One can notice peaks in the 6-6,2 area indicating the presence of substituted benzene. One can also notice peaks in the 3.8 - 4.0 area suggesting the presence of a methylene group of $-OCH_2$ from the acrylate.

Determination of the degree of alternation in the copolymer

These results obtained from a 0,5% W/V of the polymers with chloroform as a solvent were put in a graphical form - Fig.4. All the U.V. measurements were taken after six minutes of reaction. Six minutes was selected as our standard reference reaction time.

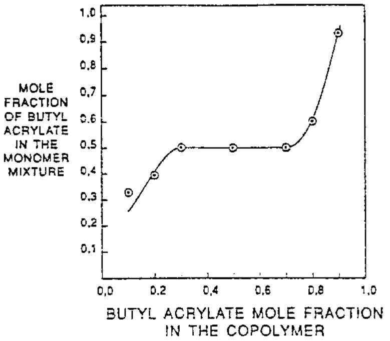


FIG. 5
MOLE FRACTION OF BUTYL ACRYLATE IN THE MONOMER MIXTURE vs MOLE FRACTION OF BUTYL ACRYLATE IN THE COPOLYMER

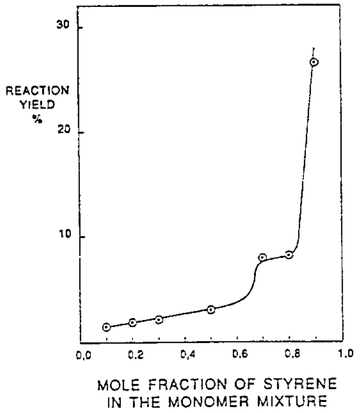
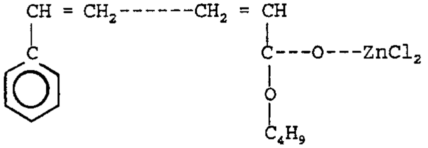


FIG. 6
REACTION YIELD vs INITIAL CONCENTRATION OF STYRENE

As the intensity of the carbonyl group is a function of the quantity of acrylate in the copolymer, the absorption curve reaches a plateau for molar fractions of butyl acrylate between 0,4 and 0,7 indicating that we have a copolymer with 50% mole of butyl acrylate.

If one plots - Fig.5 - the mole fraction of butyl acrylate in the initial monomer mixture vs moles fraction of the butyl acrylate in the copolymer, here again, a plateau shows up at a composition of between 0.3 and 0.7 in the monomer concentration. This suggest again the presence of an alternating copolymer of 50% molar composition of butyl acrylate and styrene.

The polymerization mechanism might proceed through a mechanism similar to the one suggested for methyl methacrylate and styrene (20).



The large increase of the absorption band of the carbonyl group at 0.93 and 1.54 mu with higher mole fraction of butyl acrylate and the solubility trials indicating that there is no homopolymer present and that a non-alternating structure would be present as either non equimolar block or as long sequences of non equimolar units. The mechanism would be similar to the homopolymerization of acrylonitrile complexed with $ZnCl_2$[4].

i.e.: Bu A^+ -----$\bar{B}$u A - $ZnCl_2$

In Fig.6, the reaction yield is plotted against the moles of styrene in the initial monomer mixture while keeping the butyl acrylate - $ZnCl_2$ ratio constant. One notices that there is an exponential increase in the yield to reach 26.4% conversion after six minutes of polymerization for mole ratios of 0.1, 0.1 and 0.9 of butyl acrylate, $ZnCl_2$ and styrene respectively.
If the butyl acrylate polymerization would have proceeded completely through a ternary complexation mecanism one would have obtained a yield of only 23,2% of the copolymer. Thus the complexation mechanism cannot fully explain the experimental data and it may proceed through a combination of both a complexation and a coordination mecanism.

The reactivity ratios of the polymerization were also determined by the method of triangles and this gave for r_1, the butyl acrylate reactivity ratio, a value of 0.1, the same as for r_2, styrene reactivity ratio and 0.01 for $r_1\ r_2$ suggesting again the presence of an alternating polymer.

Conclusion

It has been shown that when butyl acrylate is mixed at -20°C with $ZnCl_2$ a complex is formed. This complex reacts with styrene by a coordination mechanism.

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 through a two way mechanism: first an alternating copolymerization followed by an homopolymerization on the same polymer chain. In other words the final polymer is constituted of an alternate copolymer and of a "polymer part constituted essentially of styrene". The polymerizations may be conducted in the presence of water however it affects negativity the final conversion. The reactivity ratios for the two monomers of the system were found to be identical at 0.1.

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