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Alternating copolymerization of acrylate and isobutylene

I. Polymer synthesis and characterization

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Abstract

This paper examines the copolymerzation of methyl acrylate (MA) and isobutylene (IB) with a complexed initiating system of $AlEtCl_2$ and benzoyl peroxide (BPO). The effects of monomer ratio, monomer concentration, initiator composition and polymerization conditions on copolymer composition, degree of alternation, intrinsic viscosity and conversion were studied. An alternating copolymer was obtained when the [IB]/[MA] mole ratio was equal or greater than one.

Introduction

Since Hirooka (1) synthesized alternating copolymers of acrylonitrile and alkenes using $AlEtCl_2$ as a complexing agent, there have been numerous publications concerning alternating copolymerization of electron donating and accepting monomers in the presence of Lewis acid (2, 3). The structural regularity of an alternating copolymer results in various unique properties. Alternating copolymerization has been briefly investigated in a Chinese industrial research laboratory (4). However, only recently have Chinese research papers been published on this subject (5). The rapid growth of the Chinese chemical industry has resulted in an increased availability of isobutylene and other monomers. This study characterizes an alternating copolymer of methyl acrylate (MA) and isobutylene (IB), prepared with an initiating system consisting of $AlEtCl_2$ and benzoyl peroxide (BPO).

Experimental

Materials

MA (>99.9%, Dongfang Chemical Plant, Beijing) was distilled under nitrogen at reduced pressure and then dried over 5A molecular sieves. IB (>99.0%, Shengli Chemical Plant, Beijing) was dried by passing through a column filled with solid KOH pellets. BPO (Beijing Chemical Plant, Beijing) was recrystallized twice from ethanol and dissolved in toluene to form a 0.10 mole/l solution. Toluene (Beijing

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Chemical Plant, Beijing) was first dried over 5A molecular sieves and then distilled over sodium wire.

Polymerization

In a set order, MA, $AlEtCl_2$ and BPO were added to a solution of IB in toluene in a 125 ml glass bottle under N_2. The bottle was sealed and then placed in a constant temperature bath for a given period of time after which a 1% solution of HCl in methanol was added to stop the polymerization and to precipitate the polymer. The polymer was filtered, washed with ethanol and dried in a vacuum oven at 50℃ to constant weight.

Polymer Characterization

The intrinsic viscosity of the copolymer was measured by using a Ubbelodhe viscosimeter with 1.0-1.5g/dl toluene solution at 30.0±0.1℃ . Copolymer composition was analyzed using a CarloErba 1160 elemental analyser.The Shimadzu 421 Infrared, Varian EM 3601 NMR (for ^1H-NMR) and Spectrospin AC-80 NMR (for ^{13}C-NMR) were used to characterize the structure of the copolymer.

Results and Discussion

Type and Concentration of Lewis Acid

Upon complexation of a Lewis acid and an electron donor, the electron pair of the monomer is polarized thus the electron donating ability of the monomer increases. In this study the Lewis acids examined were, $AlEt_2Cl$, $AlEt_{1.5}Cl_{1.5}$, $AlEtCl_2$ and $AlCl_3$. The results showed that $AlCl_3$ was not effective while $AlEtCl_2$ was the most efficient for initiating the copolymerization.

Further experiments with various concentrations of $AlEtCl_2$ showed, see Table 1, that above a certain value of $[AlEtCl_2]/[MA]$, say 0.05, a very high conversion was obtained within 4 hours at 50℃. The $AlEtCl_2$ concentration has no effect on the copolymer composition. However, the intrinsic viscosity of the copolymer decreased slightly as the $AlEtCl_2$ concentration increased.This indicates that the main role of $AlEtCl_2$ is to activate the decomposition of the BPO initiator.

The effects of temperature and aging in the preparation of the $\{AlEtCl_2\text{-}MA\}$ complex were studied. Many such complexes cited in the literature have been prepared and were found to be effective at low temperatures(6). However, in this system temperatures from -70℃ to room temperature were used to produce equally effective complexes.

BPO Concentration

The fact that BPO is the initiator in this system is shown by the reciprocal relation between [BPO] and $[\eta]$ of the polymer, and by the great effect of BPO concentration on the rate of polymerization and molecular weight of the polymer. The results in Table 2 show that conversions reached only 26% after 20 hours at 50℃ in the absence of BPO. However, in the presence of BPO under the same conditions, almost 100% conversion was reached after 4 hours.

Table 1. The Effect of Alkylaluminium chloride

Alkylaluminium Chloride	[Al]/[MA] Mole Ratio	Conversion %	$[\eta]$ dl/g
$AlEt_2Cl$	0.01	0	-
	0.05	0	-
	0.10	33.0	0.360
	0.20	13.6	0.344
$AlEt_{1.5}Cl_{1.5}$	0.01	3.4	-
	0.05	64.1	0.526
	0.10	65.1	0.420
	0.20	34.6	0.380
$AlEtCl_2$	0.01	2.3	-
	0.05	96.3	0.653
	0.10	97.7	0.619
	0.20	98.8	0.580

Polymerization conditions; [MA]=1.25 mole/l., [IB]/[MA]=2.0
[BPO]/[MA]=0.01, Temperature 50℃, Time 4 Hrs.

Table 2 The Effect of [BPO] on Polymerization

[BPO]/[MA] Mole Ratio	Conv. %	[MA] Mole% In Copolymer	$[\eta]$ dl/g	Polym.Time Hours
0.000	26.2	48.9	0.940	20
0.000	0	—	—	4
0.001	76.2	48.7	1.060	4
0.005	100	50.4	1.000	4
0.010	100	48.9	0.953	4
0.020	99.8	47.6	0.832	4

Polymerization conditions; [MA]=1.25 mole/l., [IB]/[MA]=2.0
$[AlEtCl_2]$/[MA]=0.10, Temperature 50℃.

It has been reported (7) that at 55℃ in toluene BPO has a $k_d = 1.14\times10^{-6}\ s^{-1}$ which corresponds to a half life of greater than 100 hours. However, in this study the polymerization was initiated quite effectively by BPO at that comparatively low temperature. This indicated that the activation energy of BPO decomposition was lowered in the presence of $AlEtCl_2$ and that the concentration of active species was increased.

Polymerization Time and Temperature

Polymerization temperature affects the rate of polymerization and the molecular weight of the polymer. As shown in Figure 1, the rate of polymerization increases and the intrinsic viscosity of the polymer decreases with an increase in polymeization temperature. The reaction time affectes the conversion but had little or no effect on the intrinsic viscosity or copolymer composition as shown in Figure 2.

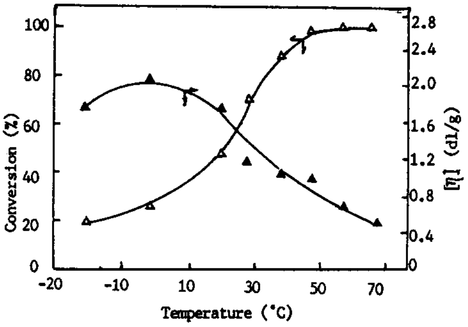

Figure 1. Effect of Temperature on Polymerization

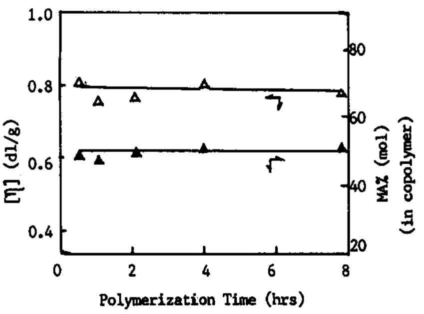

Figure 2. Effect of Polymerization Time on Polymerization

Monomer Concentration and Monomer Ratio

The monomer concentration was found to affect the conversion but not the composition, as shown in Table 3. For instance, at [IB]/[MA]=2, the copolymers all contain 50 mole% MA.

Table 3. The Effect of Monomer Concentration

[MA] Mole/l.	Conversion %	[MA] Mole% In Copolymer	[η] dl/g
1.67	95.8	50.2	0.70
1.25	93.0	48.9	0.60
1.00	85.9	50.3	0.60
0.72	73.2	48.9	0.75
0.50	64.8	47.4	0.60

Polymerization conditions; [IB]/[MA]=2.0, $[AlEtCl_2]$/[MA]=0.10 [BPO]/[MA]=0.005, Temperature 50℃, Time 4 Hrs.

The monomer ratio was found to be an important varialble and experiments were carried out to investigate its effect on copolymer composition. The results are shown in Table 4. When [IB]/[MA]>1, a copolymer with equal molar composition was obtained. However, when [IB]/[MA]<1, the copolymer was rich in MA.

Table 4 The Effect of [IB]/[MA] Ratio on Polymerization

[IB]/[MA] Mole Ratio	MA Mole% In Monomer	Yield[g] Calc.*	Yield[g] Found	MA Mole% In Polymer	[η] dl/g
10/1	9.1	3.90	3.80	49.2	1.04
5/1	16.7	3.90	3.80	48.2	0.89
3/1	25.0	3.90	4.00	48.5	0.91
2/1	33.3	3.90	3.70	49.6	0.88
3/2	40.0	3.90	4.00	47.8	0.77
5/4	44.4	3.90	3.90	48.4	0.65
1/1	50.0	3.90	2.90	51.9	0.68
1/2	66.7	1.95	1.30	55.0	0.49
1/5	83.7	0.78	1.10	76.0	0.39
0/1	100.0	0.00	1.00	100.0	--

Polymerization condition; [IB]/[MA] variable, [MA]=1.25 mole/l., [AlEtCl$_2$]/[MA]=0.10, [BPO]/[MA]=0.10, Temperature 50℃, Time 4 Hrs.

* Calculation assuming that MA combines with IB to produce a maximum yield of equal molar MA-IB copolymer.

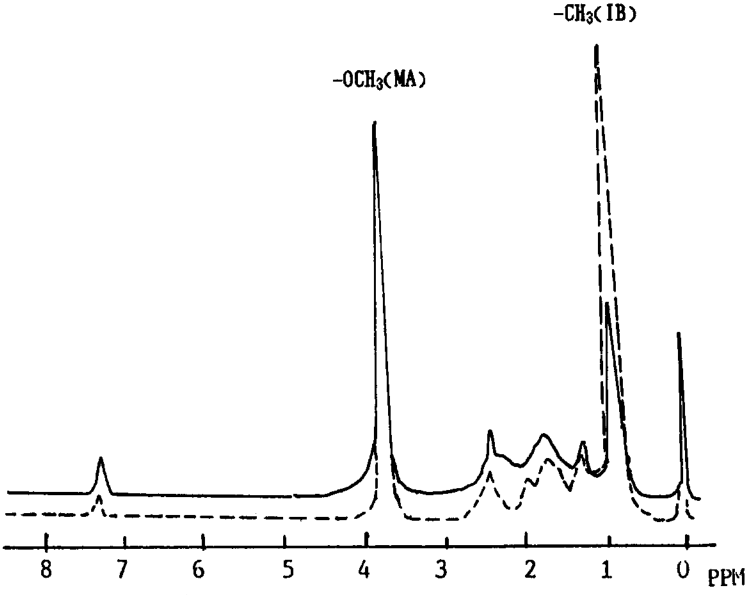

Figure 3. ^{1}H-NMR Spectra of MA-IB Copolymers
— Containing MA 76% ----Containing MA 50%

Structure Characterization of Copolymer

After some preliminary examination of the copolymer composition by elemental analysis, the sequential structure of the copolymer was characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopies.

(1) ^{1}H-NMR Analysis

The ^{1}H-NMR spectra of the copolymers having 50 and 76 mole % MA contents are shown in Figure 3. The chemical shifts and peak areas of $-CH_3$ in IB and $-OCH_3$ in MA show noticeable changes between these two copolymers.

(2) ^{13}C-NMR Analysis

The ^{13}C-NMR spectrum of the copolymer containing 50 mole % MA is shown in Figure 4. The chemical shifts and their assignments, together with data taken from the published literature (8, 9) on this IB-MA alternating copolymer are listed in Table 5.

Table 5 ^{13}C-NMR Chemical Shifts of IB-MA Copolymer

C-1	C-2	C-3	C-4	C-5	C-6	Ref.
26.00-26.58	48.00-48.46	37.19	34.28	178.39	51.39	8
26.00-26.58	35.00	37.20	40.00	180.00	48.00-52.00	9
24.11, 24.44	48.08, 46.47	35.29	32.36	176.38	49.98	Current

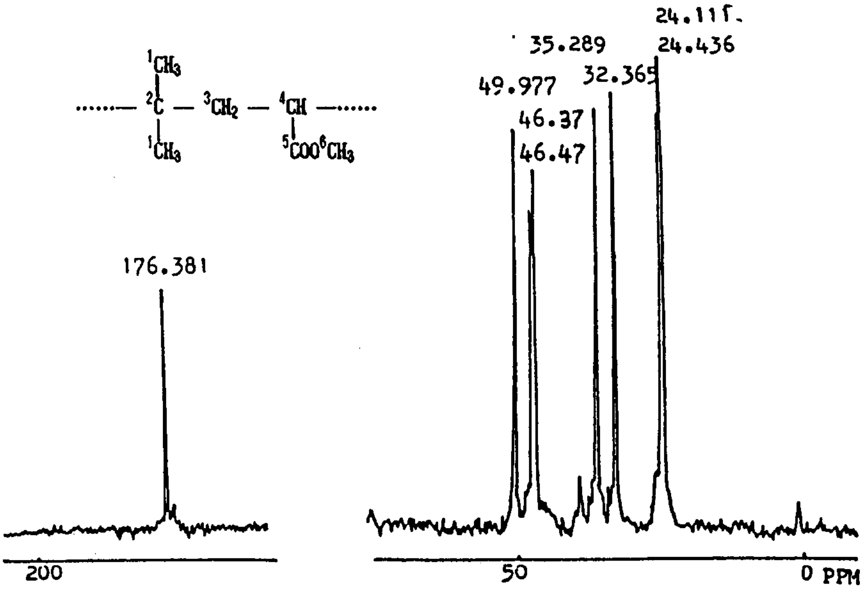

Figure 4 ^{13}C-NMR Specturm of MA-IB Alternating Copolymer Solvent, $CDCl_3$.

Results obtained in this study are in good agreement with those listed in reference (8). The 2 ppm shift difference between these two sets of data is due to the different internal standards, HMDS versus TMS, used in the two NMR analyses. The spectrum of an IB-MA copolymer containing 76 mole % MA is shown in Figure 5. The split of the carbonyl peak at d=172 ppm in comparison with the alternating copolymer spectrum shown in Figure 4, and the three additional peaks at d=39.16 ppm, 40.97 ppm and 45.09 ppm indicate the existence of MA blocks. These data suggest that when the composition of the copolymer is equal molar ratio, the copolymer is an alternating copolymer. However, when the MA content in the copolymer is greater than 50 mole % a copolymer consisting of random MA-IB sequences, together with MA blocks is obtained.

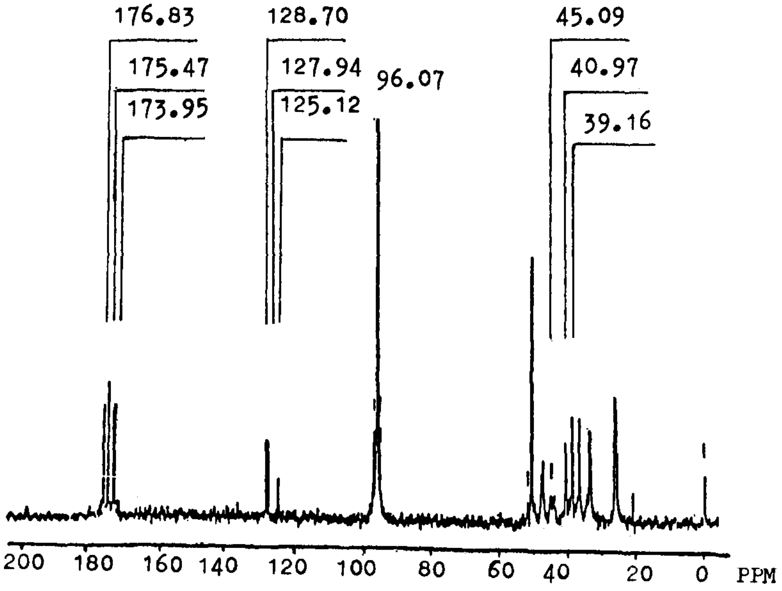

Figure 5 ^{13}C-NMR Spectrum of MA-IB Random Copolymer

Conclusion

Methyl acrylate and isobutylene can be copolymerized within a wide temperature range in the presence of AlEtCl$_2$ with BPO as the initiator. When [MA]>[IB] the copolymer is a random copolymer containing MA blocks. When [IB]≫[MA] an alternating copolymer is obtained.

The conditions for obtaining an alternating copolymer are; [MA]=0.8-0.2 mole/l, [IB]/[MA]≫1, [AlEtCl$_2$]/[MA] = 0.04 - 0.10, [BPO]/[MA] = 0.002 - 0.010, temperature 30-50℃, time 4-8 hours to conversions of 70-100%. The alternating copolymer have intrinsic viscosities in the range of 0.4-2.0 dl/g in toluene solution.

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