and confirmed by the ^{13}C-NMR spectrum of ^{13}C-labeled oligomers[10]).

The P_r values of the corresponding oligo- and polymerization of 2-IP and the polymerization of α-methylstyrene under similar conditions (Li^+, THF/−78 °C) were found to be 0.91[8] and 0.64[9c], respectively. The three systems are thus similar in that predominantly syndiotactic polymer is formed. On the other hand, the polymerization of 2-vinylpyridine leads to predominantly isotactic polymers, and that of 4-vinylpyridine results in random stereochemistry.[11] The difference in stereochemistry between the latter monomers is probably at least partially due to the intramolecular chelation of the counterion with the nitrogen lone pair of the penultimate asymmetric center, occurring in the case of 2-vinylpyridine. Such an interaction is not possible for 4-vinylpyridine. The predominantly syndiotactic content observed for the polymers derived from the three isopropenyl isomers indicates that the mechanism of oligo- and polymerization is quite different and may be largely influenced by steric factors.[9,12] It is, however, clear from the significantly higher syndiotactic content of poly(2-IP) and poly(4-IP) compared to that of poly(α-methylstyrene) that other factors are involved arising from the presence of the heteroatom in the ring. Intramolecular cation coordination of the type discussed above is not plausible on steric grounds. Thus the presence of the methyl group on the penultimate asymmetric center effectively prevents such an interaction. It is more likely that dipolar interactions between monomer and chain end are involved, especially in the case of 2-IP. In view of the relatively small differences in activation energy between the three systems, however, the nature of these interactions is difficult to identify.

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Registry No. 2,4-Dimethyl-2,4-di(4-pyridyl)pentane, 87461-72-1; 2,4,6-trimethyl-2,4,6-tri(4-pyridyl)heptane, 87461-73-2; 2,4,6,8-tetramethyl-2,4,6,8-tetra(4-pyridyl)nonane (isomer 1), 87461-74-3; 2,4,6,8-tetramethyl-2,4,6,8-tetra(4-pyridyl)nonane (isomer 2), 87461-75-4; 2,4,6,8,10-pentamethyl-2,4,6,8,10-penta(4-pyridyl)undecane (isomer 1), 87461-76-5; 2,4,6,8,10-pentamethyl-2,4,6,8,10-penta(4-pyridyl)undecane (isomer 2), 87507-90-2; 2,4,6,8,10,12-hexamethyl-2,4,6,8,10,12-hexa(4-pyridyl)tridecane, 87494-47-1; poly(4-isopropenylpyridine), 87461-77-6.

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Oligomerization of Vinyl Monomers. 13. Anionic Oligomerization of 2- and 4-Isopropenylpyridine. Stereoselectivity on Monomer Addition and Methylation Determined by End-Group ^{13}C Labels

Kazuhiko Hashimoto[1] and Thieo E. Hogen-Esch*

Department of Chemistry, University of Florida, Gainesville, Florida 32611.
Received September 14, 1982

ABSTRACT: The anionic oligomerization of 2-isopropenylpyridine (2-IP) and 4-isopropenylpyridine (4-IP) was carried out by initiation using the lithium salts of 2- and 4-isopropylpyridine, followed by termination with ^{13}C-enriched methyl iodide. From the ^{13}C NMR spectroscopic analyses of the ^{13}C-enriched terminal methyl carbons, the stereoselectivity on methylation and monomer addition of both oligomeric anions was found to be predominantly racemic-like (~80–90%), decreasing slightly with increasing degree of polymerization. The observed stereoselectivity is apparently not due to intramolecular chelation of the counterion by the pyridyl nitrogen atom but appears to be mainly caused by steric effects at the terminal carbanion. Thus, nonbonded interactions between the methyl and pyridine groups bonded to the carbanion and to the penultimate asymmetric center are expected to lead to a preferred conformation in which the *pro*-racemic face of the carbanion is most accessible to electrophilic attack.

Introduction

Several recent studies have been concerned with the stereochemistry of oligomerization of vinylpyidines,[2,3] acrylates,[4] and other vinyl monomers.[5] For the stereochemistry of anionic oligomerization of 2- and 4-vinylpyridines in THF, the apparent stereoselectivity observed in the oligomerization–methylation sequence of 2-vinylpyridine (predominantly isotactic-like) was concluded to be due to intramolecular chelation of the alkali metal cation and the nitrogen lone pair of the penultimate 2-pyridine ring.

On the other hand, anionic oligomerization of 2-isopropenylpyridine (2-IP) and 4-isopropenylpyridine (4-IP) under similar conditions yielded predominantly syndio-

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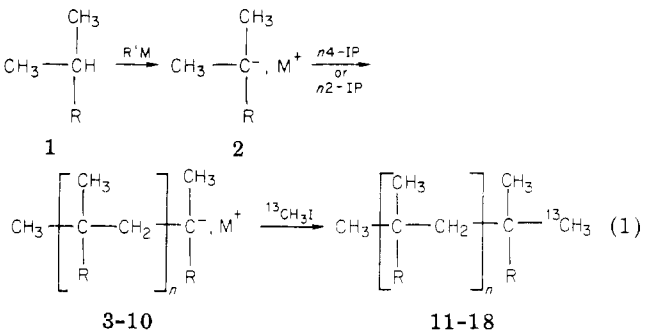


3-10 11-18

3, **11**, n = 1; **4**, **12**, n = 2; **5**, **13**, n = 3
6, **14**, n = 4; **7**, **15**, n = 5; **8**, **16**, n = 6
9, **17**, n = 7; **10**, **18**, $n \cong 50$
a, R = 2-pyridyl; b, R = 4-pyridyl

tactic-like oligomers (eq 1), although minor amounts of other stereoisomeric oligomers were also detected.[6,7] However, quantitative data regarding the distribution of stereoisomers could not be obtained due to limitations imposed by the use of ^{1}H NMR and the stereochemical complexity of at least the higher oligomers.

It was found, however, that the ^{13}C-NMR absorption of the terminal methyl group in oligomers **13** and **14** was sensitive to the stereochemistry of the two preceding dyads. By using ^{13}C-enriched methyl iodide as electrophile, therefore, if might be possible to obtain detailed information regarding the stereochemistry of both methylation and vinyl addition as a function of chain length.

Experimental Section

Purification of materials, preparation of Li initiators, and oligomerizations were carried out in a high-vacuum system as described in the preceding paper.[7] The Cs initiator was prepared by reacting the 1,1,4,4-tetraphenylbutane dianion cesium salt (prepared by reacting 1,1-diphenylethylene with Cs metal in THF) with 1.1 equiv of 2- or 4-isopropylpyridine in THF at −78 °C. ^{13}C-enriched methyl iodide (Merck, purity 90%) was diluted with methyl iodide to 15.4% ^{13}C content, followed by drying over calcium hydride on the vacuum line.

The resulting crude oligomers were separated by preparative liquid chromatography with an Altex Model 332 programmable gradient system.[7] ^{13}C-NMR spectra were recorded on a JEOL Model JNM-FX-100 Fourier transform high-resolution spectrometer at 25 MHz at room temperature with Me_4Si as a reference.

The stereochemistry of methylation and vinyl addition was calulated by a comparison of labeled and unlabeled spectra. Nuclear Overhauser effects on the relative intensities of the methyl absorptions were previously shown to be small but should not play a role here since the calculations are based upon the "calibrated" spectra of the unlabeled compounds. The same is the case for the method of evaluation of intensities obtained from peak heights. Errors in absorption intensities are estimated as less than 5%. The assignment of the f_1' and f_2' absorptions in Figure 2 were confirmed by spectra of the meso tetramer and its mixtures with the racemic isomer.

Results and Discussion

After anionic oligomerizationof 4-IP at −45 and −78 °C in THF, the resulting oligomeric anions were terminated at the same temperatures with ^{13}C-enriched methyl iodide. The resulting oligomers **11**–**18** were separated with a Merck Lobar preparative column, and obtained as white solids by the method previously reported.[7]

The ^{13}C-NMR spectra of the trimer, tetramer, and pentamer of 4-IP are shown with those of the corresponding oligomers formed by termination with unlabeled methyl iodide in Figures 1–3, respectively.[8] In the spectra of oligomers terminated by unlabeled methyl iodide, the main peaks are assigned to the syndiotactic-like isomers;[7]

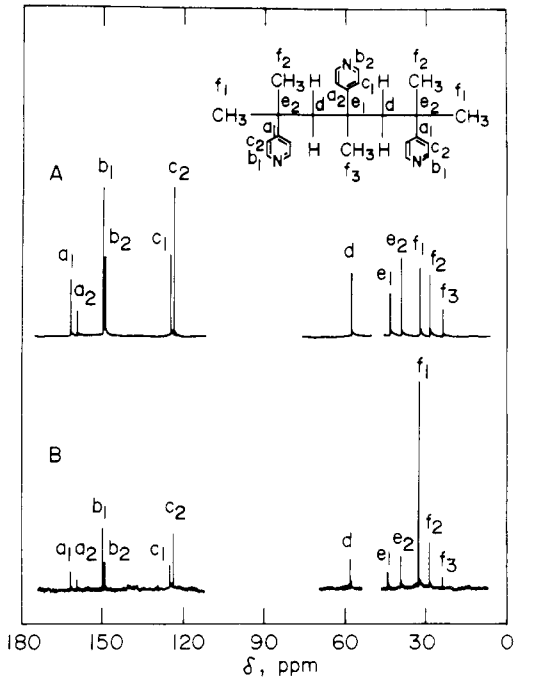


Figure 1. ^{13}C-NMR spectra of 4-IP trimer in methanol-d_4. Room temperature, 25 MHz. A, trimer prepared by termination of the trimeric anion with methyl iodide; B, trimer prepared by termination with ^{13}C-enriched methyl iodide.

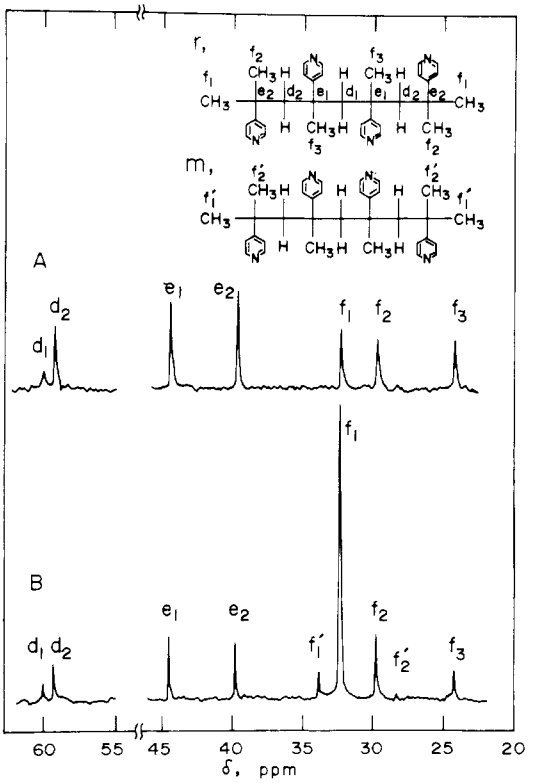


Figure 2. ^{13}C-NMR spectra of 4-IP tetramer in methanol-d_4. Room temperature 25 MHz. A, tetramer prepared by termination of the tetrameric anion with methyl iodide; B, tetramer prepared by termination with ^{13}C-enriched methyl iodide.

it was difficult to detect, with high reproducibility, any peaks due to other stereoisomers such as the meso tetramer and the heterotactic pentamer because of their relatively small proportions.

From the figures, it is apparent that the methylations in these reactions are stereoselective. For instance, in Figure 1B the ratio of the absorptions of the diastereotopic

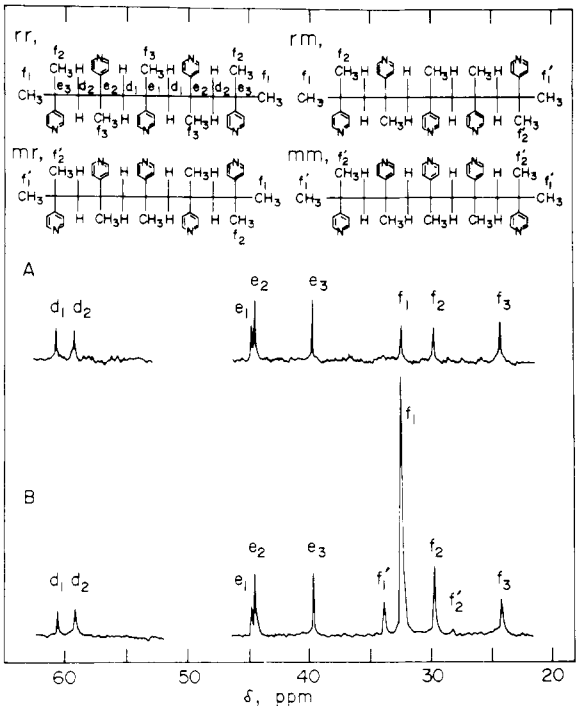


Figure 3. ^{13}C-NMR spectra of 4-IP pentamer in methanol-d_4. Room temperature, 25 MHz. A, pentamer prepared by termination of the pentameric anion with methyl iodide; B, pentamer prepared by termination with ^{13}C-enriched methyl iodide.

methyl groups f_1 and f_2 is much higher than in Figure 1A. In contrast to the previous paper, the stereochemical assignment of the labeled diastereotopic methyl groups is of interest. We define as racemic- and meso-like the labeled methyl groups that are in positions stereochemically analogous to the corresponding CH_2 groups bonded to the reactive center as a result of racemic or meso monomer addition. The downfield absorption is most plausibly assigned as racemic-like, since the meso-like methyl group would be more strongly shielded in the all-trans conformation demonstrated by X-ray analysis for the 2-IP tetramer.[6]

The degree of methylation stereoselectivity may be readily determined by using the equations

$$c_{f_1} = P_r q + 1.11(1 - P_r) \quad (2a)$$

$$c_{f_2} = (1 - P_r)q + 1.11P_r \quad (2b)$$

leading to

$$P_r = (c_{f_1} - 1.11)/(q - 1.11) \quad (3)$$

where c_{f_1} and c_{f_2} are the ^{13}C atom percentages in terminal methyl end-group positions f_1 and f_2, q and 1.11 are the ^{13}C atom percentages in the enriched and regular methyl iodide, respectively, and P_r is the probability for a racemic-like placement of the labeled methyl group. c_{f_1} and c_{f_2} are determined by the equations

$$I_{f_1}/I_{0,f_1} = (1.11 + c_{f_1})/2.22 \quad (4a)$$

$$I_{f_2}/I_{0,f_2} = (1.11 + c_{f_2})/2.22 \quad (4b)$$

where I_{f_1} and I_{0,f_1} are the intensities of peak f_1 relative to a suitable other carbon atom (such as e_2 in Figure 1) in the trimer terminated with enriched and regular methyl iodide, respectively.

Figures 2 and 3 clearly show that the ^{13}C NMR spectrum of the methyl end groups is also dependent upon the stereochemistry of the penultimate dyad. Two absorptions f_1' and f_2' downfield from f_1 and upfield from f_2 are both attributable to the meso tetramer and appear to be assignable to the racemic- and meso-like methyl group, respectively. The ratios f_1/f_2 and f_1'/f_2' are nearly identical. The stereoselectivities of methylation for the racemic and meso anion hence appear to be similar.[9] No further splitting to antepenultimate dyads is observed in Figure 3, and all four pentamer absorptions appear to have essentially the same chemical shifts as in the tetramer. Assuming the stereoselectivities of methylation to be the same for the case of anions flanked by racemic and meso dyads, we can write for the oligomers **13–18**

$$I_{f_1}/I_{f_1'} = (1.11P_{r,i} + c_{f_1}P_{r,t})/(1.11P_{m,i} + c_{f_1'}P_{m,t}) \quad (5)$$

where $P_{r,i}$ ($P_{m,i}$) and $P_{r,t}$ ($P_{m,t}$) are the fractions of first and final racemic (meso) monomer placements, respectively, and all other symbols have their previously defined meaning. Assuming now that $P_{r,i}$ is the same for the series of oligomers [$P_{r,i} \neq F(n)$], it may be calculated for the tetramer (where $P_{r,i} = P_{r,t}$) so that $P_{r,t} = 1 - P_{m,t}$ can be determined as a function of the degree of oligomerization. Using peaks f_1 and f_2, the same may be done for the stereoselectivity of methylation of anions flanked by racemic dyads. Oligomers **11a–17a** having ^{13}C-enriched terminal methyl groups were prepared, separated, and analyzed by procedures similar to that employed for 4-IP oligomers (Figure 4).

The results for the 2-IP and 4-IP oligomers, together with some of the corresponding polymers prepared in the presence of other cations, are given in Table I. Several trends should be noted. First, as observed with poly(α-methylstyrene)[10–12] both 2-IP and 4-IP oligomers and polymers are highly syndiotactic. The methylation likewise appears to occur in highly racemic-like fashion, especially in the case of the 2-IP oligomers. Second, there is no major dependence of stereochemistry on chain length, with the possible exception of the higher oligomers of 4-IP. Third, there is no significant effect of temperature or counterion on the stereochemistry, at least in the cases reported.

These observations are in contrast to that in the case of the oligomerization of 2- and 4-vinylpyridines (2- and 4-VP). In this case, the stereochemistry of formation of the 2-VP oligomers and 4-VP oligomers is different. Thus, the 2-VP oligomers were found to be predominantly isotactic-like,[2] whereas the 4-VP oligomers appeared to be stereochemically random.[13] For the 2-VP oligomers, moreover, the stereoselectivities of methylation and monomer addition are quite different and highly dependent upon counterion. In this case, it was shown that the results are consistent with an intramolecular coordination of the counterion with the nitrogen lone pair of the penultimate pyridine group. The present results are inconsistent with the presence of an intramolecularly chelated carbanion and suggest the predominance of steric factors in determining oligomerization stereochemistry.

Thus, racemic placements appear to be energetically favored due to pyridine–pyridine nonbonded interactions, and this is also indicated from CPK space-filling models. Such models also indicate that the all-trans conformation may be favored, and indeed such a conformation has been shown by X-ray techniques to exist for the 2-IP tetramer. Moreover, the NMR spectra, especially that of the broadened and strongly shielded interior methyl groups, provide further evidence for such a conformation.

An interpretation of these results should focus on the nature of the reactive intemediates. Conductance measurements of lithio- and sodio-2-ethylpyridine yield dissociation constants in the 10^{-8}–10^{-10} M^{-1} range.[2d,15] Dissociation of the "living" polymers should have the same magnitude or less.[14] Accordingly, ionization into free an-

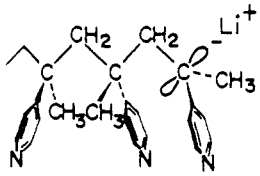
Table I
Stereoselectivity on Methylation and Last Monomer Addition of 4-IP and 2-IP Oligomeric Anions[a]

resulting oligomer	countercation	temp, °C	probability of racemic placement on methylation[e] 4-IP	2-IP	probability of racemic placement on last monomer addition[e] 4-IP	2-IP
trimer	Li	−45	0.88			
trimer	Li	−78	0.89	0.95		
tetramer	Li	−45	0.82		0.88	
tetramer	Li	−78	0.86	0.99	0.90, 0.90[b]	0.91, 0.89[b]
pentamer	Li	−45	0.88		0.86	
pentamer	Li	−78	0.86	0.94	0.87	0.90
hexamer	Li	−45	0.77		0.81	
hexamer	Li	−78	0.78	0.98	0.80	0.88
heptamer	Li	−78		0.99		0.86
octamer	Li	−78		0.99		0.86
polymer[d]	Li	−78			0.78[b,c]	0.85[b,c]
polymer[d]	K	0-25			0.72[b,c]	
polymer[d]	Cs	−78				0.80[b,c]

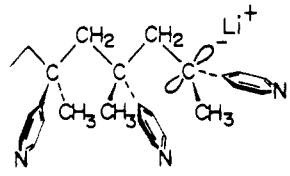
[a] Estimated from the peak intensity ratio in the ^{13}C-NMR spectra using eq 2-5. [b] Estimated from the peak intensity ratio in the ^{1}H-NMR spectra. [c] Calculated from the distribution triad as determined by ^{1}H NMR of the α-methyl group.[7,17] [d] Calculated molecular weights 50 000-200 000. [e] Error estimated as ±5%.

ions should be 0.1% or less at the concentrations of living polymers in these systems (10^{-1}–10^{-2} M). Moreover, addition of highly dissociated lithium tetraphenylboride in the case of the polymerization of 2-IP initiated by Li salts has not significantly affected the stereochemistry of polymerization. Conductance studies on 4-pyridyl carbanions have shown that these salts tend to be even less dissociated.[16] Therefore, it is plausible that the propagating carbanion chain end is in the form of ion pairs and perhaps a small fraction of higher aggregates such as triple ions.

The carbanions in these systems have been shown by ^{1}H and ^{13}C NMR to be delocalized and sp^2-hybridized carbanions.[2d] Structures such as 18 and 18′ representing



18



18′

the chiral ion pairs in which the counterion is associated with the *pro*-racemic and *pro*-meso face of the carbanion, respectively, would therefore be most plausible.

It appears that 18 should be favored over 18′ because of carbanion–pyridine–pyridine nonbonded interactions in 18′. This is especially the case since the charge is substantially delocalized into the pyridine moiety as shown in earlier work.[2d] This prevents rotation along the carbanion–C_2 or –C_4 bond, thus effectively giving the pyridine ring greater bulk. As a result, cation-side attack[2,3] on 18 appears predominant, producing mostly racemic dyads.

The above mechanism does not explain in detail all the results. For instance, the origin of the small differences between methylation and monomer addition and between the oligomerization stereochemistry of 2- and 4-IP is not yet clear. However, the gross features of these reactions appear to fit the proposed mechanism. Thus, the similarity between the stereochemistry of oligomerization of 2- and 4-IP and the chain length independence of the stereochemistry appears to be satisfactorily explained. The above mechanism also predicts Bernoullian polymerization statistics. Preliminary experiments with a number of cation–solvent systems appear to bear this out.[17] Furthermore, the stereochemistry of addition of the terminal monomer unit is very similar to the dyad stereochemistry of the chain as determined from triad analysis (Table I).

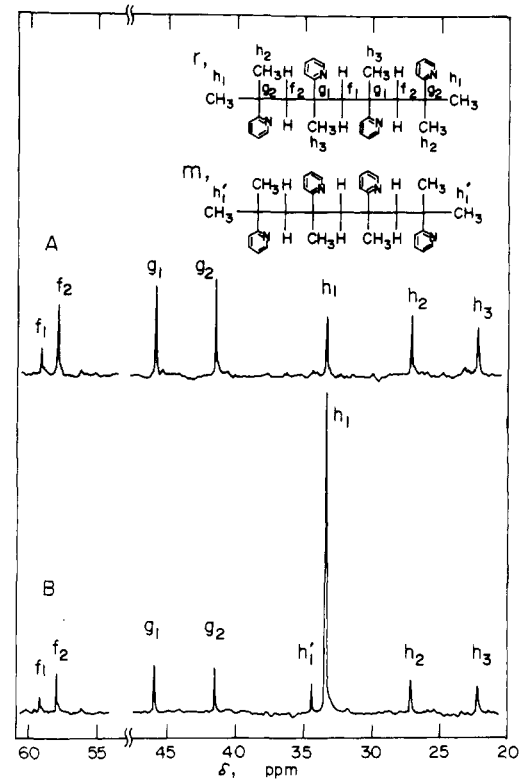


Figure 4. ^{13}C-NMR spectra of 2-IP tetramer in benzene-d_6. Room temperature, 25 MHz. A, tetramer prepared by termination of the tetrameric anion with methyl iodide; B, tetramer prepared by termination with ^{13}C-enriched methyl iodide.

Such a similarity is consistent with Bernoullian statistics.[18] Further work on the polymerization of these monomers is in progress.

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Registry No. 2-Isopropenylpyridine, 6515-13-5; 4-isopropenylpyridine, 17755-30-5.

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Copolymerization of 2,4,5-Trichlorophenyl Acrylate with Styrene: Reactivity Ratios, Molecular Weights, and ^{13}C NMR Spectra

Boreddy S. R. Reddy, Reza Arshady, and Maurice H. George*

Department of Chemistry, Imperial College, London SW7 2AY, England.
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ABSTRACT: The free radical copolymerization of 2,4,5-trichlorophenyl acrylate (M_1) with styrene (M_2) in chlorobenzene and in the presence of α,α'-azobisisobutyronitrile (AIBN) at 60 °C is reported. ^{13}C NMR spectra of M_1, the homopolymers of M_1 and M_2, and an equimolar copolymer of M_1 and M_2 are given. Copolymer compositions of ten copolymer samples obtained from feed ratios of M_1:M_2 = 7:93 to 92:8 were determined by chlorine analysis. The reactivity ratios were estimated by the Kelen and Tudos method to obtain r_1 = 0.29 ± 0.03 and r_2 = 0.25 ± 0.03. The effect on molecular weights of initiator concentration, extent of monomer conversion, and feed composition is also discussed. The weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights were determined by gel permeation chromatography. $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ values for the homopolymers at low (~4%) conversion were 20 350 and 2.0 for M_1 and 43 700 and 1.69 for M_2. The corresponding values for a copolymer formed from an equimolar monomer concentration ($[M_1] + [M_2]$ = 0.81 mol dm^{-3}) [AIBN] = 9.08×10^{-5} mol dm^{-3}, were 25 900 and 1.83 at 7% conversion and 20 400 and 2.56 at essentially complete, 100% conversion. When the initiator concentration was increased 20-fold, the values of $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ for the above-mentioned copolymer were 10 800 and 2.30 at 8% conversion. In the presence of constant initiator concentration, the gradual increase in the ratio of M_1:M_2 (from 7:93 to 92:8) was accompanied by a decrease in molecular weights ($\bar{M}_w$ from 46 430 to 21 570) and an increase in $\bar{M}_w/\bar{M}_n$ (from 1.74 to 2.14, respectively). These findings indicate that an increase in polymer radical combination occurs as the mole fraction of M_2 in the monomer feed increases.

Introduction

Incorporation of activated acrylates or methacrylates into polymers provides one of the most versatile routes for the preparation of reactive polymers. Copolymers of activated (meth)acrylates have, for example, been employed to study kinetic aspects of macromolecular reactions,[1] preparation of macromolecular drug carriers,[2] immobilized enzymes,[3] and polymeric reagents for peptide synthesis[4a] and transition-metal catalysis.[4b] A flexibly cross-linked equimolar copolymer[5] of 2,4,5-trichlorophenyl acrylate (M_1) and styrene (M_2) has, in particular, been found ideally suitable for the preparation of a wide range of polymeric reagents and polymer supports.[4,6] Currently, we are interested in the use of linear (soluble) copolymers of M_1 and M_2 for the development of electroreactive polymers suitable for the preparation of surface-modified electrodes and electrocatalysis. Systematic studies of the copolymerization of activated (meth)acrylates have, however, not been reported in the literature, and the data of ref 2 appear to represent the only previously published information. The present report describes the free radical copolymerization of M_1 and M_2 and the evaluation of the reactivity ratios by the Kelen and Tudos method.[7] A brief analysis of ^{13}C NMR spectra, the molecular weights ($\bar{M}_w$ and $\bar{M}_n$), and the polydispersity indices ($\bar{M}_w/\bar{M}_n$) of the copolymers is also presented.

Experimental Section

Materials. 2,4,5-Trichlorophenyl acrylate was prepared as described in the literature.[2] Styrene (Aldrich) was washed with 5% sodium hydroxide and distilled under reduced pressure. AIBN (BDH) was recrystalized from chloroform. Methanol and chlorobenzene (Rose Chemicals) were used as received.

Polymerization. The calculated amounts of M_1, M_2, AIBN, and chlorobenzene (see Table I) were placed in a standard Quickfit flask, and the mixture was flushed with nitrogen for 10 min. The flask was then tightly stoppered and maintained in a water bath at 60 ± 1 °C, and the polymerization was allowed to proceed to about 10% conversion (~30–70 min).

The reaction mixture was then poured into excess methanol, and the polymer was filtered, washed with methanol, and dried under vacuum at room temperature.

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