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Initiation Reaction in the Strong Base Catalyzed Polymerization of Acrylamide

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SUMMARY:

Reaction of acrylamide with sodium alkoxides in alcoholic media was investigated. When sodium methoxide was used, β-methoxy propionamide was obtained in good yield. This alkoxide seems to initiate the polymerization of acrylamide via MICHAEL-type addition reaction. When sodium *t*-butoxide was used, reaction products having *t*-butoxyl end group and having vinyl end group were isolated and identified respectively. The polymerization initiated by *t*-butoxide seems to contain two sorts of reaction scheme; the MICHAEL-type addition reaction and the formation of acrylamide anion.

ZUSAMMENFASSUNG:

Die Reaktion von Acrylamid mit Natriumalkoholaten wurde in alkoholischer Lösung untersucht. Unter Verwendung von Natriummethylat wurde β-Methoxypropionamid in guten Ausbeuten erhalten. Dieses Alkoholat scheint die Polymerisation von Acrylamid über eine Reaktion vom Typ der MICHAEL-Addition zu initiieren. Mit Natrium-tert.-butylat wurden Reaktionsprodukte isoliert und identifiziert, die tert.-Butoxyl- und Vinylendgruppen besitzen. Die durch das tert.-Butylat gestartete Polymerisation scheint nach zwei Reaktionen abzulaufen: die Reaktion vom Typ der MICHAEL-Addition und die Bildung von Acrylamidanionen.

Introduction

It is well known that acrylamide polymerizes by strong basic catalysts to poly-β-alanine. In the polymerization reaction hydrogen-transfer is contained, so it is called by name of "hydrogen transfer polymerization"1–3).

Two different initiation mechanisms are proposed for the sodium alkoxide initiated polymerization: BRESLOW *et al.*1) obtained from polymerization mixture a solid material which was thought to be a dimer containing a vinyl group, and concluded that the predominating initiation reaction may comply with the reaction scheme represented by Eq. (1).

$$CH_2{=}CHCONH_2 + B^{\ominus} \leftrightharpoons CH_2{=}CHCON^{\ominus}H + BH \qquad (1)$$

The second initiation mechanism is proposed by OGATA3) who followed the polymerization reaction infrared spectroscopically and concluded the nucleophilic attack at the β-carbon atom to carbonyl group must be the initiation step of the polymerization reaction as shown in scheme (2).

$$CH_2{=}CHCONH_2 + B^{\ominus} \leftrightharpoons B{-}CH_2C^{\ominus}HCONH_2 \leftrightharpoons B{-}CH_2CH_2CON^{\ominus}H \qquad (2)$$

These two authors, however, could not isolate any of oligomers in a sufficiently pure state to identification. The present investigation deals with the isolation of oligomeric products of the initiation reaction catalyzed by alkoxyl anion.

In the case of sodium *t*-butoxide, the reaction product derived from scheme (1) was isolated together with that of scheme (2). The MICHAEL-type reaction product was likewise isolated in the case of sodium methoxide in good yield. The mode of initiation reaction was discussed in comparing two sodium alkoxides.

Results

With the amount of initiator increased, the degree of polymerization should be lowered. As an extreme case, stoichiometric reaction with molar ratio 1:1 and 1:2 (monomer moles to initiator moles) was carried out.

1. *Equimolar reaction of acrylamide and sodium methoxide*

The reaction was carried out in dioxan at 70 °C. A solid material which was demonstrated to contain methoxyl group was obtained.

2. *Reaction of acrylamide with a twice-fold amount of sodium methoxide*

The reaction was carried out in methanol at 60 °C. A crystalline material was obtained in considerably good yield, and it was identified to be β-methoxy propionamide ($CH_3O{-}CH_2{-}CH_2CONH_2$) by infrared absorption spectroscopy and elementary analysis.

3. *Equimolar reaction of acrylamide and sodium t-butoxide*

β-*t*-Butoxy propionamide was isolated when the reaction mixture of acrylamide and sodium *t*-butoxide at 60 °C. in *t*-butanol solvent was treated to neutralize with 2 *N*-hydrochloric acid.

Neutralization of the reaction mixture by hydrochloric acid was not satisfactory, because the anion containing vinyl group produced by the reaction scheme (1), if present, should turn back to original acrylamide which could not be distinguished with unreacted acrylamide. When the reaction was terminated by benzylchloride, the reaction products were very complicated. Some of which could be isolated by solvent extraction followed by column chromatography. These compounds were assigned by means of infrared spectroscopy, elementary analysis, and molecular weight determination to be N-benzyl-β-*t*-butoxy propionamide, N-benzylacrylamide and a dimer, having *t*-butoxyl group; N-benzyl β-(β′-*t*-butoxy propionamido)propionamide (t-$C_4H_9O-CH_2CH_2CONH-CH_2CH_2$-$CONHCH_2-C_6H_5$).

It was unsuccessful to isolate higher oligomers in pure state, but the infrared absorption spectra of the oligomer mixture indicated the presence of bands due to both alkoxyl and vinyl end groups.

Discussion

The initiation reaction of acrylamide polymerization may well be discussed with considering the different actions between sodium methoxide and sodium *t*-butoxide toward acrylamide.

1. *Reaction with sodium methoxide*

β-Methoxy propionamide was isolated from the reaction mixture in good yield (68%). This fact suggests that the nucleophilic MICHAEL-type addition of a methoxyl anion at carbon-carbon unsaturation (scheme 2) was easier than the anionic extraction of a proton from the amide group (scheme 1). No effort was made to isolate the latter products and the formation of amide anions could not be confirmed.

The polymerization of acrylamide by sodium methoxide anion seems to be predominantly initiated by the formation of the anion $CH_3O-CH_2-\overset{\ominus}{C}H-CONH_2$ at the first stage, then hydrogen transfer may take place producing β-methoxy-propionamide anion.

2. *Reaction with sodium t-butoxide*

When the reaction was terminated by benzylchloride, N-benzyl-β-*t*-butoxy propionamide, N-benzyl-β-(β′-*t*-butoxy propionamido)propionamide and N-benzylacrylamide were obtained. These products could be fractionated from the reaction mixture by alumina-column chromatography. They were identified by analysis and by infrared absorption spectroscopy. Assignment of *t*-butoxyl bands was referred to ORY[4].

The occurrence of the MICHAEL-type addition reaction was revealed from the fact that β-*t*-butoxy compound was likewise obtained in the reaction mixture terminated by 2 *N*-hydrochloric acid. One course of the propagation reaction should be that through β-*t*-butoxy propionamide anion (scheme 2), because a dimer containing *t*-butoxyl group was obtained.

On the other hand, the formation of N-benzylacrylamide was confirmed. The reaction of acrylamide with benzylchloride did not take place in the neutral media. N-Benzylacrylamide should hereby be formed in the termination process; *i.e.* acrylamide anion was neutralized by benzyl cation. Thus the initiation reaction of route (1) could not be neglected when the polymerization was catalyzed by sodium *t*-butoxide. Propagation reaction via route (1) has not been established in the present stage, but the infrared absorption spectra of partially fractionated higher oligomers suggested that these were mixtures of oligomers having vinyl and *t*-butoxyl end groups.

3. *Difference in the Catalytic Influences between Sodium methoxide and Sodium t-butoxide*

In the equimolar reaction of acrylamide and sodium methoxide, the polymerization reaction seemed to be too rapid so that a monomeric product could not be detected; only higher oligomers containing methoxyl end groups were obtained. To control the reaction in the step of monomeric state, twice-fold amount of sodium methoxide was needed. In this case the yield of the MICHAEL-type addition reaction was 68 %. From this result the initiation reaction of acrylamide-polymerization catalyzed by sodium methoxide seems to be predominated by the MICHAEL-type addition reaction (scheme 2).

Sodium *t*-butoxide reacted with acrylamide moderately; β-*t*-butoxy propionamide was obtained (31 %) in the equimolar reaction terminated by 2*N*-hydrochloric acid. At least 17 % of acrylamide ejected its amide hydrogen and formed the acrylamide anion. It may cause the propagation reaction with retention of vinyl end group. In the present experiment it was found out that the *t*-butoxyl group could be able to add to acrylamide unlike to the case of acrylonitrile[5], though the resistance to addition seemed to be more remarkable than of methoxyl anion.

The factor which controls the catalytic initiation course is not obvious in detail in the present stage whether it is electronic or steric. Additional factors such as solvent, temperature *etc.* appear to affect the initiation and propagation route, but no investigation about these factors is contained in this paper.

Experimental

1. *Reaction of Acrylamide with Sodium Methoxide*

a) Equimolar Reaction

Acrylamide was purified by sublimation at temp. below its melting i.vac.

As solvents, methanol, dioxane, and *t*-butanol were employed after purification according to the usual methods.

In 70 ml. of anhydrous dioxane 1.2 g. of metallic sodium and 50 ml. of methanol were dissolved, and then 0.05 g. of phenyl-β-naphthylamine was added. To the dioxane solution, 3.5 g. of acrylamide was added slowly with stirring, then the mixture was maintained at 70 °C. for 30 Min. After it was neutralized with 2 *N*-hydrochloric acid, the solvents were distilled off under reduced pressure, then the residue was fractionated by solvent extraction. From acetone soluble fraction 0.6 g. of acrylamide was recovered (17 %). Acetone insoluble part was divided into two fractions; ethyl acetate soluble and insoluble parts. Ethyl acetate soluble part was crystallizable by cooling (0.5 g., m.p. 150–160 °C.). By infrared spectroscopic examination, the following functional groups were detected: CH_3O- (2820 cm^{-1}), amide I (1650 cm^{-1}), amide II (1550 cm^{-1}), C–O–C (1115–1120 cm^{-1}), nitrogen content was 14.69 %. Ethyl acetate insoluble part appeared to contain higher oligomers by infrared spectroscopic examination, but no effort for further fractionation was applied.

b) Reaction with twice-fold amount of Sodium Methoxide

Into the solution of sodium (2.2 g.) in absolute methanol (50 ml.) containing 0.05 g. of phenyl-β-naphthylamine, were added drop by drop 100 ml. of methanol solution of acrylamide (3.5 g.) at room temp. with stirring, then the mixture was heated to 60 °C. and continued to stir for an hr. After neutralization with 2 *N*-methanolic hydrochloric acid, the solvent was distilled off under reduced pressure. Residual solid material was treated again with methanol, undissolved sodium chloride and small amounts of polymer were separated off, and then methanol was removed again. Treating the solid residue with ether, the ether-extracts became crystallizable. Recrystallization was carried out from ether. The substance melted at 50–50.5 °C. (3.2 g.). It showed infrared absorption at 2830 cm^{-1} (CH_3O-), 1670 cm^{-1} (amide I), and 1115 cm^{-1} (C–O–C), but there was no absorption based an amide II and unsaturated carbon-carbon bonds.

($C_4H_9O_2N$ (103.1)	Calcd.	C 46.40	H 8.63	N 14.03
	Found	C 46.59	H 8.80	N 13.58

Crystalline material obtained is probably β-methoxy propionamide. Yield: 63 %.

2. *Reaction of Acrylamide with Sodium t-Butoxide*

a) Neutralized with hydrochloric acid

Metallic sodium (1.2 g.) was added to 100 ml. of *t*-butanol, and the mixture was refluxed until all of sodium was completely dissolved. After cooling the solution to 60 °C., 0.05 g. of phenyl-β-naphthylamine and 50 ml. of *t*-butanol solution containing 3.5 g. of acrylamide was added drop by drop to it. Reaction was continued for two hrs. with stirring. The reaction mixture was neutralized with 2 *N*-hydrochloric acid, distilled off the solvent, and residual material was filtered.

i) Acetone extract of the filtrate was a yellow syrup, and it was eluted by ethyl acetate through a short (2 cm.) alumina column, then crystallizable fraction was recrystallized from ether. Yield: 2.0 g. (31 %). M.p. 73–74 °C. It showed infrared absorption at 1362 cm^{-1} (*t*-butyl), 1198, 1027, and 835 cm^{-1} (*t*-butoxyl), 1080 cm^{-1} (C–O–C) and 1665 cm^{-1} (amide I), but no absorption based on amide II group and unsaturated carbon-carbon bond was detected.

$C_7H_{15}O_2N$ (145.2) Calcd. C 57.90 H 10.41 N 9.65
Found C 57.31 H 10.43 N 9.41

It was identified to be β-*t*-butoxy propionamide (t-C_4H_9O–$CH_2CH_2CONH_2$).

ii) Acetone insoluble part was treated with ethyl acetate and the soluble part could not be crystallized. It might be an oligomer containing *t*-butoxyl group; absorption bands based on this group were detected infrared spectroscopically.

b) Neutralized with Benzylchloride

Acrylamide and sodium *t*-butoxide were treated as above mentioned in *t*-butanol for 45 min. at 60 °C. The reaction mixture was neutralized by excess benzylchloride. Neutralization reaction was needed to reflux it at the boiling temp. of *t*-butanol for 3.5 hrs. Precipitates were filtered off, and evacuated to remove most parts of *t*-butanol and of benzylchloride. The residue was extracted with acetone to separate off the precipitate which is formed again by the extraction process, and from the filtrate a yellow oily material was obtained when acetone was removed i. vac. By treatment with excess petroleum ether (b.p. 60–80 °C.) the soluble part of oily material was separated off. Oily residue is 4.3 g.

Column chromatography: The residue obtained by above process was repeatedly fractionated by column chromatography on activated alumina. Elution was carried out successively with petroleum ether, benzene, ether, ethylacetate, acetone, methanol, and formic acid. The fraction with petroleum ether seemed to contain *t*-butanol, benzylchloride, and *t*-butylbenzylether followed by three minor portions of separated bands which were unidentified but found to be some ester type materials having a sharp absorption at 1735 cm^{-1} in the infrared spectra.

In the fraction eluted by benzene, two compounds were isolated. One of which was colorless oil eluted more rapidly, and it was purified by repeating chromatography until it showed a constant refractive index (n_D^{18} = 1.5090). Yield: 0.75 g. By determination with infrared spectroscopy, groups of amide I (1660 cm^{-1}), of amide II (1555 cm^{-1}), of *t*-butoxyl (1365 cm^{-1}, 1195 cm^{-1}, 1030 cm^{-1}, 835 cm^{-1}), of C–O–C (1080 cm^{-1}) and of mono-substituted benzene (735 cm^{-1}, 695 cm^{-1}) was detected, but none of absorption based on carbon-carbon unsaturation was found.

$C_{14}H_{21}O_2N$ (235.3) Calcd. C 71.49 H 8.94 N 5.96 Mol.-wt. 235
Found C 70.95 H 8.94 N 5.85 Mol.-wt. 236

Molecular weight was determined by Rast method. It might be N-benzyl-β-*t*-butoxy propionamide (t-C_4H_9O–$CH_2CH_2CONHCH_2C_6H_5$). This fraction corresponded to at least 6% of original acrylamide.

The second elution band of benzene was crystallizable. Purification was carried out by repeated chromatography followed by recrystallization with ether. Colorless plates of m.p. 73–74 °C. were obtained (1.33 g.). *t*-Butoxyl groups were not detected by infrared spectroscopy, but absorptions at 1620 cm^{-1} and 955 cm^{-1} were based on the vinyl end group. Absorption at 995 cm^{-1} was the same origin as that of original acrylamide. Absorptions of amide I (1655 cm^{-1}), of amide II (1540 cm^{-1}), and of mono-substituted benzene (745 and 695 cm^{-1}) were present. Elementary analysis agreed with N-benzylacrylamide.

$C_{10}H_{11}ON$ (161.2) Calcd. C 74.51 H 6.88 N 8.69 Mol.-wt. 161
Found C 74.06 H 6.92 N 8.27 Mol.-wt. 164

Molecular weight was determinated by Rast method. This fraction corresponded to at least 17% of original acrylamide.

The first band eluted by ether was N-benzylacrylamide described above, and the fraction eluted later by ether contained a very small portion of β-*t*-butoxy acrylamide together with original acrylamide (0.28 g.).

The fraction eluted by ethyl acetate could be crystallized by repeated chromatography. It was recrystallized from the mixture of ethyl acetate-ether (70:30 v/v) to colorless needles of m.p. 98–98.5 °C. Yield was 0.57 g. Molecular weight was determined to be 292 (calcd. 306) and it is supported to be dimeric. By infrared spectroscopy, absorptions based on amide I, amide II, *t*-butoxyl group and mono-substituted benzene were detected but any of absorption based on vinyl group was not found out, and its spectra resembled to that of N-benzyl-*t*-butoxy acrylamide except of rather complication. Elementary analysis agreed with N-benzyl-β-(β′-*t*-butoxy-propionamido)propionamide.

$C_{17}H_{26}O_3N_2$ (306.4) Calcd. C 66.64 H 8.55 N 9.14
Found C 66.41 H 7.74 N 8.99

This fraction corresponded to at least 4% of original acrylamide.

The higher oligomers were eluted from more polar solvents such as acetone, methanol, and formic acid, but none of the fractions could be crystallized in pure state; the initial fraction of methanol elution solidified (m.p. 123–126 °C.) but it seemed to be a mixture of oligomers having two or three monomer units. Infrared spectroscopy of it showed to be a mixture of vinyl and ether types.

3. *Reaction of Acrylamide and Benzylchloride in Neutral Media*

In 50 ml. of benzylchloride containing 0.02 g of phenyl-β-naphthylamine, 3.5 g. of acrylamide was suspended under vigorous stirring. The mixture was heated up to 85 °C. for 3.5 hrs., acrylamide was recovered quantitatively.

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