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Studies on the addition reaction of diethylamine to multiacrylate catalyzed by lithium diethylamide

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Summary

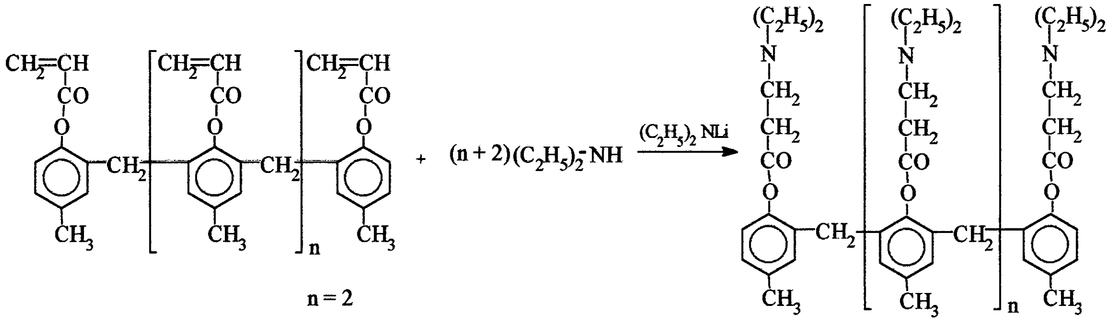
The nucleophilic addition reaction of diethylamine to vinyl groups of multiacrylate - oligo[(2-acryloyloxy-5-methyl-1,3-phenylene)methylene] and to p-cresyl acrylate as model compound were investigated. The reaction was carried out in benzene with excess amine in the presence of lithium diethylamide as catalyst within the temperature range from 21 to 50°C. Based on the obtained results, it has been shown that the addition reaction rate of diethylamine to multiacrylate and p-cresyl acrylate is proportional to $[CH_2=CH-]$ and to $[Et_2NLi]$ with the ratio $[Et_2NH]_o/[Et_2NLi]_o = 5$. Second-order addition reaction rate constants and activation energies for the systems under investigation have been determined. The chemical composition of the resultant addition products has been confirmed by spectroscopic methods: IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis.

Introduction

As shown in the literature reports, the addition reactions of primary and secondary amines to vinyl double bonds of monomers have aroused numerous interests (1-8). Imai et al. (1) investigated the addition reaction of diethylamine to the styrene vinyl group catalyzed by lithium diethylamide with the ratio $[(C_2H_5)_2NH]_o\ /[(C_2H_5)_2NLi]_o > 2$. They have shown that this is a second-order reaction and its rate is proportional to concentrations of styrene and catalyst. Investigating the addition reaction of diethylamine to butadiene in the presence of lithium diethylamide with the ratio $[(C_2H_5)_2NH]_o\ /[(C_2H_5)_2NLi]_o = 3$, Narita et al. (2) have found that this is a stereospecific reaction since 1-diethylamino-cis-butene-2 stereoisomer is formed in 99%. Based on kinetic and spectroscopic measurements, the authors have concluded that 1:2 complex consisting of lithium diethylamide and diethylamine is the operating species in this addition reaction. Mechanism of the reaction addition secondary amine with styrene and butadiene were alredy described (2,3). The addition reactions of primary and secondary alkylamines to

1,4-divinylbenzene and 1,3-divinylbenzene result in new monomers (4,5), while the polyaddition reactions of N,N'-diethylethylenediamine or piperazine to 1,4-divinylbenzene in the presence of appropriate lithium amide give macromonomers with amine groups (6,9). Polymeric amines obtained by polymerization such monomers and macromonomers have various promising applications of such as ion exchangers, flocculants, anticorrosive cationic paints or biocompatible materials (10).

In this work, we examined the kinetics of the lithium diethylamide catalyzed addition reaction of diethylamine to the vinyl double bonds of multiacrylate (Scheme 1) and to p-cresyl acrylate as model compound in order to elucidate the mechanism and synthesis of a new type of tertiary oligomeric amine.



Scheme 1

The quaternarization of such an amine with alkyl halides should result in quaternary ammonium salts which may find their application as catalysts in organic syntheses (11).

Experimental

Materials

p-Cresol was purified by distillation under reduced pressure. Diethylamine (DEA) was refluxed over CaH_2 under a nitrogen atmosphere and then distilled. n-Butyllithium (n-BuLi) commercial product 2M solution in pentane was used as received. Benzene was distilled over CaH_2 and stored over 4A molecular sieves. Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride. p-Cresyl acrylate (p-CA) was distilled under reduced pressure. p-Cresol-formaldehyde (p-CF) resin was obtained by polycondensation of p-cresol with formaldehyde according to the procedure described by of Kämmerer (12). p-CF resin was fractionated by precipitation with water - ethanol (1:1 vol%) of fractions from acetone-ethanol solution (3:1 vol%). For futher experiments, one of the fraction were chosen with molecular weight measured cryoscopically of M_n = 458 g/mol.

Synthesis of multiacrylate (MA) - oligo[(2-acryloiloxy-5-methyl-1,3-phenylene) methylene]

The chosen fraction of p-CF resin was then esterified according to procedure given in the literature (12). Molecular weight of MA measured cryoscopically was M_n = 714 g/mol. ^{1}H-NMR ($CDCl_3$): δ = 2.10-2.28 (d,3H,CH_3), 3.59-3.78 (m,2H,CH_2), 5.41-6.79 (t,3H,CH_2=CH), 6.92-7.18 (m,2H,ArH). ^{13}C -NMR ($CDCl_3$): δ = 20.4 (CH_3), 30.9 (CH_2), 121.8, 127.3, 135.6, 145.1, 146.5 (CAr), 129.7, 130.9 (CH= CH_2), 163.4 (C=O). IR (cm^{-1}) 1740 (C=O); 1634 (CH_2=CH). Anal. Calcd for $C_{11}H_{11}O_2$ (175.1) C, 75.38%; H, 6.33%, Found: C, 75.68%; H, 6.14%.

Addition reaction of DEA to MA and p-CA

The typical procedure of the addition reaction was as follows: To a thermostated glass reactor (30 mL) provided with a magnetic stirring rod, nitrogen inlet and a rubber stopper, 0.15 mol of DEA in 5.8 mL of benzene was introduced. The solution was cooled down to a temperature of 0°C and then 0.03 mol of n-BuLi was added be means of a syringe through the rubber stopper. The mixture was stirred for 15 min. to form lithium diethylamide. Then, the solution temperature was raised up to the experiment-predetermined value and 4 mL of benzene solution containing 0.06 mol of MA (calculated per a single vinyl group) was added be means of the syringe. The reaction course was controlled at determined intervals by sampling the reaction solution and recording its IR spectra. The quantitative changes in amine concentration in the samples were determined by analyzing the intensity of stretching vibration absorption band of secondary amine >NH bond at 6470 cm^{-1} (13), using a previously prepared calibration curve. After several dozen hours, the addition reaction of amine to vinyl double bonds was completed. Then, the solution was concentrated under vacuum at a temperature of 30°C and the product was precipitated in heptane, purified by double dissolution in chloroform and precipitation in heptane and finally dried in a vacuum drier at 50°C. ^{1}H-NMR ($CDCl_3$): δ = 0.87 [s,6H,$(CH_3)_2$], 2.13 (s,3H,ArCH_3); 2.47 [s,6H,$CH_2N(CH_2)_2$], 3.75 (s,4H,CH_2 and ArCH_2Ar), 7.08 (d,2H, ArH). ^{13}C-NMR (DMSO-d_6): δ = 10.4 (CH_3), 20.5 (ArCH_3), 33,4 (ArCH_2Ar); 45.5 [$\underline{C}H_2N(\underline{C}H_2)_2$]; 48.4 ($\underline{C}H_2CO$); 124.1-154.1 (CAr); 174.2 (C=O). IR (cm^{-1}): 1740 (C=O); 1461 (N-CH_2) Anal. Calcd for $C_{17}H_{22}O_2N$ (248.2) C, 72.52%; H, 8.90%; N, 5.60%, Found: C, 71,68%; H, 8.45%; N, 5.38%.

Measurements

Infrared spectra were recorded using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) instrument. ^{13}C- and ^{1}H-NMR spectra were obtained using a Bruker DPX 250 MHz spectrometer with $CDCl_3$ as solvents and TMS as an internal reference.

Results and Discussion

From our preliminary examinations it follows that the addition reaction of DEA with vinyl groups of MA and with p-CA takes place only in the presence of catalytical quantities of lithium diethylamide and without any side reaction such as vinyl polymerization.

In order to obtain quantitative information on the addition reaction of DEA with vinyl groups of MA as well as with p-CA, kinetic studies were carried out.

The dependence of initial MA vinyl group concentration (from 0.05 to 0.13 mol/L, calculated per a single vinyl group) on the reaction rate is shown in Fig. 1. Since the first-order plot stays linear until 25% conversion, the reaction rate is proportional to the MA vinyl group concentration, while the coresponding dependence for the p-CA is linear up to about 50% conversion (Fig. 1). Thus, in further consideration, the scope of interpretation was limited to the initial stage of the process. The pseudo first-order rate constants, calculated as the slopes of straight lines in Fig. 1, for the examined systems are listed in Table 1.

Table 1. Pseudo first-order rate constants k' of the reaction of Et_2NH-Et_2NLi complex with vinyl group of MA and with p-CA at 30°C.

$[Et_2NH]_o$ mol/L	$[Et_2NLi]_o$ mol/L	$[CH_2=CH-]_o$ mol/L	MA k' h^{-1}	p-CA k' h^{-1}
0.3	0.06	0.05	0.81	0.72
0.3	0.06	0.10	0.83	0.74
0.3	0.06	0.13	0.82	0.71

In order to determine the dependence of the reaction rate on the concentration of lithium diethylamide, the reaction rate was analyzed at a constant initial concentration of $CH_2 = CH$-groups of MA and p-CA at the ratio of $[Et_2\ NH]_o$ to $[Et_2NLi]_o$ being 5. When the reaction rate υ is expressed as in Eq. (1) the pseudo first-order rate constant k can be determined from the slope of the straight the lines in Fig. 2.

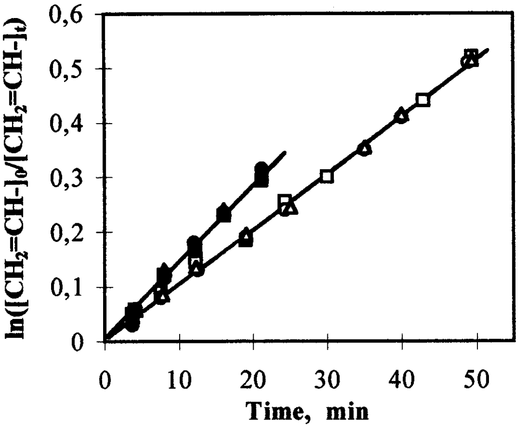


Fig.1. First-order analysis of the reaction of Et_2NH-Et_2NLi complex with MA (—) and with p-CA (---); dependence of MA and p-CA concentration; $[Et_2NLi]_o$=0.06 mol/L, $[Et_2NH]_o/[Et_2NLi]_o$= 5 in benzene at 30°C; $[CH_2=CH\text{-}]_o$ = 0.05 mol/L (△ ▲), 0.10 mol/L (□ ■) and 0.13 mol/L (o ●)

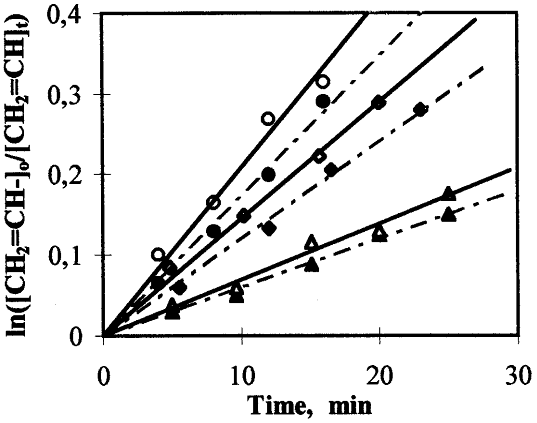


Fig.2. First-order analysis of the reaction of Et_2NH-Et_2NLi complex with MA (—) and with p-CA (---); dependence of $[Et_2NLi]_o$; $[CH_2=CH\text{-}]_o$ = 0.1 mol/L, $[Et_2NH]_o/[Et_2NLi]_o$ = 5 in benzene at 30°C; $[Et_2NLi]_o$= 0.03 mol/L (△ ▲), 0.06 mol/L (□ ■) and 0.09 mol/L (o ●)

$$\upsilon = k' [CH_2 = CH\text{ -}] \qquad (1)$$

The slope of the lines which are obtained from the plot of ln k' *vs.* ln $[Et_2NLi]_o$, for of MA and for p-CA, should show the dependency on the lithium diethylamine concentration:

$$k' = k\,[Et_2\,NLi]^x \qquad (2)$$

As the slope of the lines in Fig. 3 are x = 1 the reaction rate can be expressed as Eq. (3):

$$\upsilon = k\,[CH_2 = CH\text{ -}]\,[Et_2\,NLi] \qquad (3)$$

The determined values of second-order rate constants for the addition of DEA to MA containing four monomer units and to low-molecular-weight p-CA within the temperature range 21 - 50°C are listed in Table 2. These data were used to prepare Arrhenius plot of 1n k *vs.* 1/T (Fig. 4). The activation energy values calculated from the slopes of straight times are given in Table 2.

As follows from the data in Table 2, the rate constants of DEA addition to MA as well as to model p-CA increase with raising temperature from 21 to 50°C, which is consistent with the general principles of the conventional kinetics. Moreover, the addition reaction of secondary amine to the vinyl groups of oligomeric MA is slightly faster than that of p-CA addition, thus, for example, at 50°C k = 8.40 x 10^{-3} L/mol· s for MA, while k = 8.06 x 10^{-3} L/mol· s for p-CA. The same order of magnitude of rate constants has been found by Narita et al. (3) for DEA to styrene addition k = 1.6 x 10^{-3} L/mol· s and to

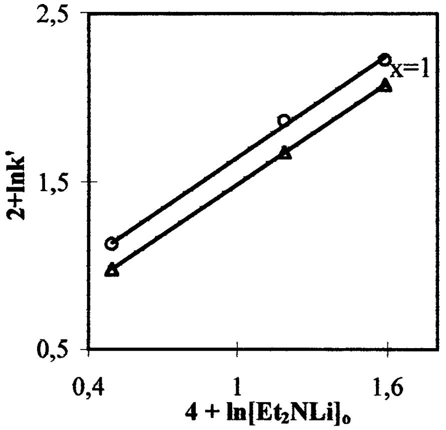


Fig.3. Relationship between lithium diethylamide concentration and pseudo first-order rate constant for of MA (o) and p-CA (Δ); $[Et_2NH]_0 / [Et_2NLi]_0 = 5$, $[CH_2{=}CH\text{-}]_0 = 0.1$ mol/L in benzene at 30°C

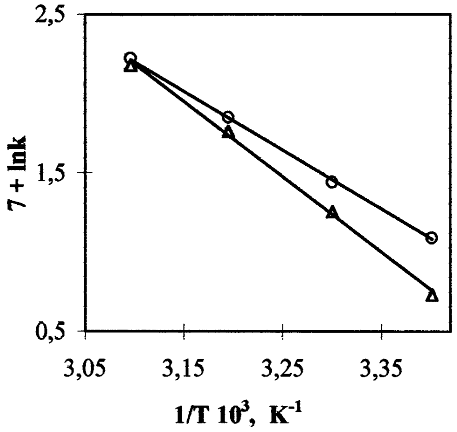


Fig.4. The Arrhenius plot for reaction of addition $Et_2NH\text{-}Et_2NLi$ complex with MA (o) and p-CA (Δ)

Table 2. Values of the second-order rate constants k at various temperature and activation energy E_a for addition reaction of $Et_2NH\text{-}Et_2NLi$ complex with vinyl group of MA as well as with p-CA[a]

Sample	Temp. °C	k x 10^3 L/mol·s	E_a kJ/mol
multiacrylate	21 30 40 50	2.29 3.86 5.80 8.40	35.80
p-cresyl acrylate	21 30 40 50	1.90 3.40 5.30 8.06	39.40

[a] Reaction conditions: $[CH_2{=}CH\text{-}]_0 = 0.1$ mol/L, $[Et_2NLi]_0 = 0.06$ mol/L, $[Et_2NH]_0 / [Et_2NLi]_0 = 5$ in benzene

butadiene k = 1.4 x 10^{-3} L/mol· s in cyclohexane at 50°C. Slight differences are also observed in the activation energy values of these reactions (Table 2). The slight increase in the reaction rate of DEA addition to MA compared to that its addition to p-CA may be associated with higher local concentration of vinyl groups in the reaction system of oligomeric MA. The effect of local concentration of side functional groups linked to a polymer chain has been suggested in paper (14).

Based on the performed kinetic analysis and literature data (2,3), the general scheme of DEA addition to p-CA as a model compound may therefore be depicted as follows:

$$Et_2NLi + 2Et_2NH \rightarrow Et_2NLi \cdot 2Et_2NH \qquad (4)$$

$$Et_2NLi{\cdot}2Et_2NH + CH_2{=}CH\text{-}COO\text{-}C_6H_4\text{-}CH_3 \rightarrow Et_2NHCH_2CHLiCOO\text{-}C_6H_4\text{-}CH_3 \cdot 2Et_2NH \qquad (5)$$

$$Et_2NHCH_2CHLiCOO\text{-}C_6H_4\text{-}CH_3 \cdot 2Et_2NH + Et_2NH \rightarrow$$
$$Et_2NCH_2CH_2COO\text{-}C_6H_4\text{-}CH_3 + Et_2NLi \cdot 2Et_2NH \qquad (6)$$

The addition of amine to α,β unsaturated ester takes place as a result of the attack of nucleophilic agent, diethylamine-lithium diethylamide complex, on carbon atom at β position showing an electron deficit which is due to electron acceptor properties of carbonyl group and the conjugation of vinyl group with carbonyl group (15). In the case of oligomeric, four monomeric unit acrylate, the DEA addition proceeds gradually according to equations (5) and (6) resulting in a 100% conversion of vinyl groups.

The product thus obtained is a slightly yellowish powder, soluble in ethanol, chloroform, THF, acetone, but insoluble in hexane and water. The structure of the addition product - oligo[2-{(3-N,N-diethylaminopropionic)-5-methyl-1,3-phenylene} methylene] was characterized by IR, ^{1}H and ^{13}C-NMR. The spectroscopic measurements have confirmed that the product is an oligoamine possessing diethylamine group at one end of each monomeric unit. Fig. 5 (A) and (B) shows an example of ^{1}H-NMR spectra of initial MA and the addition product, respectively. In the comparison to the MA spectrum, the addition product spectrum shows no multiplet signal of CH_2=CH- protons within the range 5.75 - 6.65 ppm, which indicates that all of them were used in the addition reaction. On the other hand, new broadened proton signals of added $-CH_3$ and $-CH_2-$ groups are observed with maxima at 0.95 ppm and 2.53 ppm, respectively.

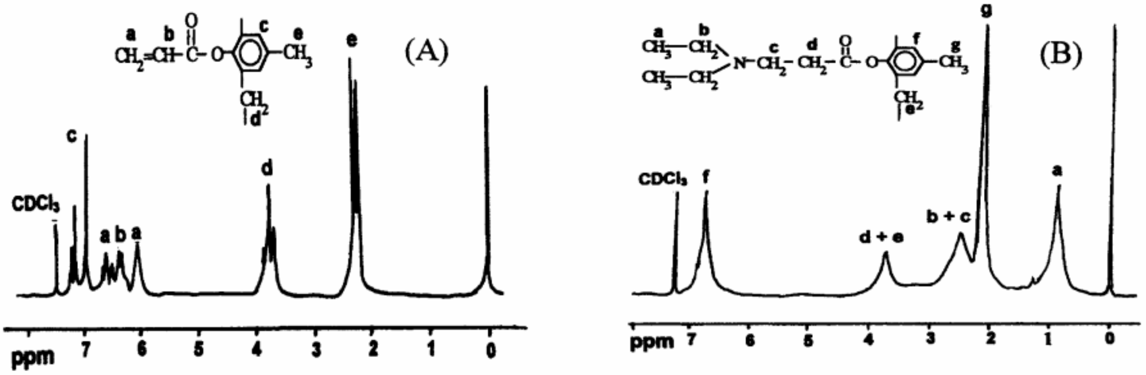


Fig. 5. The spectra ^{1}H-NMR of MA (A) and addition product (B)

The presence of tertiary amine groups in the oligomeric addition product makes it possible to synthesize quaternary ammonium salts in the reaction with alkyl halides which can be used as catalyst in organic syntheses. This issue will be the subject of further studies.

Conclusion

The studies performed show that the reaction of diethylamine addition to vinyl double bonds of MA and to p-CA takes place in the presence of lithium diethylamide as catalyst with excess amine. The addition reaction rate is proportional to [CH_2=CH-] and to [Et_2NLi] with the ratio [Et_2NH]$_o$/[Et_2NLi]$_o$ = 5. The obtained oligomer has tertiary amine groups at one end of each monomeric unit.

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