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Interracial Polyfunctional Condensation: ATR Study on Polyfunctional Interfacial Condensation

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INTERFACIAL POLYFUNCTIONAL CONDENSATION: ATR STUDY ON POLYFUNCTIONAL INTERFACIAL CONDENSATION

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ABSTRACT

The behavior in the interfacial polycondensation of 4,4'-methylene dianiline (MDA) and ethylene diamine (EDA) in water with 1,2,4,5-benzenetetra acyl chloride (BTAC) in dichloromethane with tetrabutyl ammonium chloride (TBAC) as the catalyst was examined with ATR, ^{1}H NMR, a pH meter, and ESCA. As the BTAC is a tetrafunctional compound with high reactivity, the interfacial polycondensation reaction of BTAC and the diamine is a complicated reaction involving the competitive reaction of hydrolysis and amidation. ATR was employed for analyzing the change in the chemical structure on both sides of the interfacial layer during the reaction. A clear description of the reaction process was made. The interface reaction of this system takes place in the organic phase, and the reaction is diffusion-controlled. It is clear that the film grows toward the organic phase from the interface region until the reaction is over. When sodium carbonate or TBAC is added, the chemical structure of the top and bottom sides formed by interfacial polycondensation is quite different. TBAC assists the transfer of diamine from the water phase to the organic phase, and once TBAC links with diamine, the presence of hydrochloride will not damage their linkage.
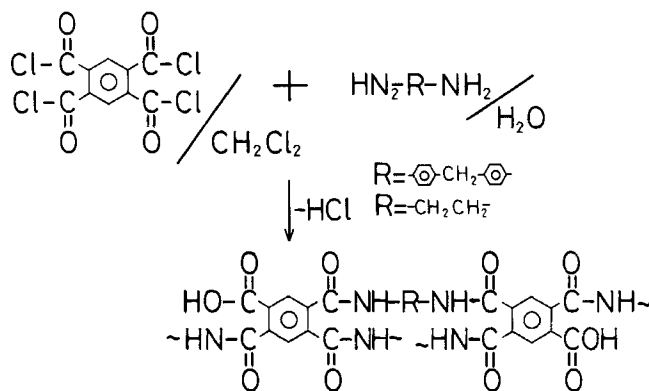
SCHEME I.

INTRODUCTION

Attenuated total reflectance (ATR) is often described as a technique for examining the surface of materials, such as thin films or opaque solids [1]. In a typical ATR experiment, an evanescent IR beam penetrates into the specimen to a depth of 0.1 μm. Therefore, the full range of properties to a depth of 0.1 μm is measured as an average. Since ATR penetrates deeper than other facial analysis instruments, such as ESCA, Auger, or SIMS (these penetrate to a thickness of about 0.01 μm), ATR analytical results do not display the facial characteristics well. Nevertheless, ATR analysis provides information on functional groups of film which is not easily attained by other methods.

In a previously published paper we studied the interfacial polycondensation of BTAC and diamine. A typical reaction scheme for this is shown in Scheme I [2]. How the reaction conditions affect the hydrolysis of the film was also described.

It has been reported that the interfacial polycondensation of difunctional groups is a complex reaction [3–8]. Therefore, it is hard to actually measure dynamic data of interfacial polycondensation reactions of monomers with polyfunctional groups due to their more complicated features. Consequently, we attempted to understand the process of interfacial polyfunctional condensation through this research. We set different reaction conditions and employed ATR for analyzing the chemical structures on both sides of the film during the reaction.

EXPERIMENTAL

Reagents and Solvents

4,4'-Methylene dianiline (MDA) was recrystallized from isopropyl alcohol. Ethylene diamine (EDA) was distilled at normal pressure before being used. Dichloromethane was dried with 4A molecular sieves and stored over molecular sieves until use. BTAC was synthesized as in a previous paper [2]. All the solvents used were purified in the usual manner. All other reagents were of analytical grade.

Characterization

A Perkin-Elmer 1760-X FTIR spectrophotometer was used to record the spectra of KBr pellets. In a typical experiment, 20 scans per sample were averaged.

^{1}H-NMR spectra were recorded on an AM-300 WB FT-NMR spectrometer using TMS as the internal standard and CDCl$_3$ or D$_2$O as the solvent. Chemical shift (δ) is given in parts per million.

ATR spectra were obtained on a Bomen DA 3.002 FTIR instrument at 2 cm^{-1} resolution, with KRS-5 used as an internal reflection element. Strips of supported film 5 × 0.5 cm^2 were placed inside the ATR cell on each side of the crystal (KBS-5) so that the film surface was in contact with the crystal face. In a typical experiment, 100 scans per sample were averaged.

ESCA spectra were obtained with a Perkin-Elmer PHI 1605 spectrometer using MgK$_\alpha$ radiation, and the Au$_{4f\,7/2}$ level at 83.8 eV binding energy was used for calibration purposes.

We designed a descend–ascend controlling instrument with 10 μm precision for precise control of the ascending and descending distance in order to secure the electrode and move it to the position required. A RADIOMETER PHM 82 standard pH meter was used to record the pH of the solution, using a RADIOMETER G242C electrode as an indicator electrode and a RADIOMETER K401 electrode as a reference electrode.

Variation of pH on the Interface

We took 0.0005 mol aniline and dissolved it in 100 mL aqueous solution. Then we took 0.0005 mol BTAC and dissolved it in dichloromethane. First, we used a 10-mL pipet to transfer the BTAC solution into a

30-mL beaker, and then we moved the pH electrode to 0.3 cm from the surface. The pH electrode was attached to a vertical positioning instrument with 10 μm precision. Next, we used a 10-mL pipet to take up the aniline solution and injected it onto the surface of the BTAC solution along the lining walls of the container. Then we immediately moved the pH electrode downward and recorded the pH value. In our experiment the distance was adjusted to 10 μm each time. We attempted to understand the variation of pH on the interface region.

pH Measurement

First, we used a 10-mL pipet to transfer the BTAC solution into the beaker, and then moved the pH electrode to 0.3 cm from the surface. Next we used a 10-mL pipet to take up the diamine solution and inject it onto the surface of the BTAC solution along the lining walls of the container. We immediately moved the base of the pH electrode to the interface position and recorded the pH value versus time. The change in pH value acquired is directly related to the rate of reaction; i.e., the more the pH changes with reaction time, the faster the rate of the interfacial reaction.

Interfacial Polycondensation

We dissolved the required amount of BTAC in dichloromethane and the diamine in water. In experiments with the BTAC–EDA system, the concentration of the BTAC solution was equal to the concentration of the EDA solution, i.e., 0.061 M. In experiments with the BTAC–MDA system, the concentration of the BTAC solution was also equal to the concentration of the MDA solution, i.e., 0.000504 M. We used a 10-mL pipet to take 40 mL of the BTAC solution and place it into the bottom of a Teflon dish. The Teflon dish was placed on the bottom of a beaker 9 cm in diameter. As the Teflon dish was about 4 cm from the interface, it did not affect the reaction of the interface. Then we used a 50-mL syringe to take 40 mL of the diamine solution and we injected it onto the surface of the BTAC solution along the lining walls of the container. We set the required reaction conditions (as shown in Table 1). After the required time, we pulled up the Teflon dish to hold the film produced by the reaction, thus enabling both sides of the film to remain in a stable position. The film was first immersed in 0.001 N NaOH(aq) for the first rinsing, and then it was submersed in dichloromethane for the second

TABLE 1. Condition of Interfacial Polymerization

| | Water phase | |
Notation	TBAC, g/10 cm^3	NA$_2$CO$_3$, g/10 cm^3
UCUB	0	0
2 CLUB	0.02	0
UCB	0	0.265

rinsing, three times for each rinsing. After it was air-dried and vacuum-dried, the films required for further analysis on ATR could be obtained.

Relationship between TBAC and Diamine

The aqueous solution was divided into three 0.1 wt% MDA of 100 cm^3 each: the 0.022 g TBAC was added to the first, the second was the same but with 0.2 mL of 0.01 N HCl(aq) added after the 0.022 g TBAC was added, and the third had 0.1 N HCl(aq) added before the 0.022 g TBAC. We placed these three separately onto three 100-mL portions of dichloromethane which were placed into three 500 mL beakers. We then let these rest for 1 h to allow diffusion. Then we used a 30-mL syringe to pump out the solution at the lower level and vacuum dried it. The solid powder obtained was dissolved in CDCl$_3$ for ^{1}H-NMR analysis. It can be noted from the above analysis that the results obtained are the same even if we omit the diffusion procedure, so the EDA and TBAC were directly dissolved in D$_2$O for ^{1}H-NMR analysis.

RESULTS AND DISCUSSION

Variation of pH on the Interface

As indicated in Fig. 1, the thickness of the interface layer was less than 10 μm. More precise measurement is required to determine the thickness of the interface layer.
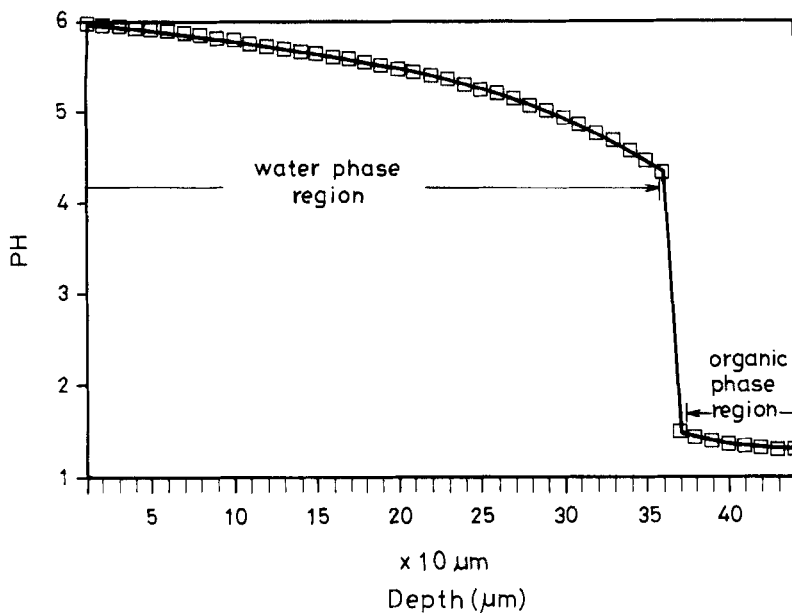
FIG. 1. pH measurement at successive points near interface, staring in the water phase region and descending below the interface region to the organic phase region.

Interfacial Condensation

In the BTAC–EDA System

As shown in Fig. 2, the chemical structures of the two sides of the films appear to be quite different when TBAC and sodium carbonate are added. The chemical structure depends on whether the reaction region of the interfacial polycondensation is in the organic phase or in the water phase. The chemical structure of the surface of the films adjacent to the water phase shows markedly more characteristic absorption of the amide group [9, 10] [IR(KBr) cm^{-1}: 1540, 1640]. The chemical structure of the face of the films adjacent to the organic phase shows the characteristic absorption of the acid group [11, 12] [IR(KBr) cm^{-1}: 1720].

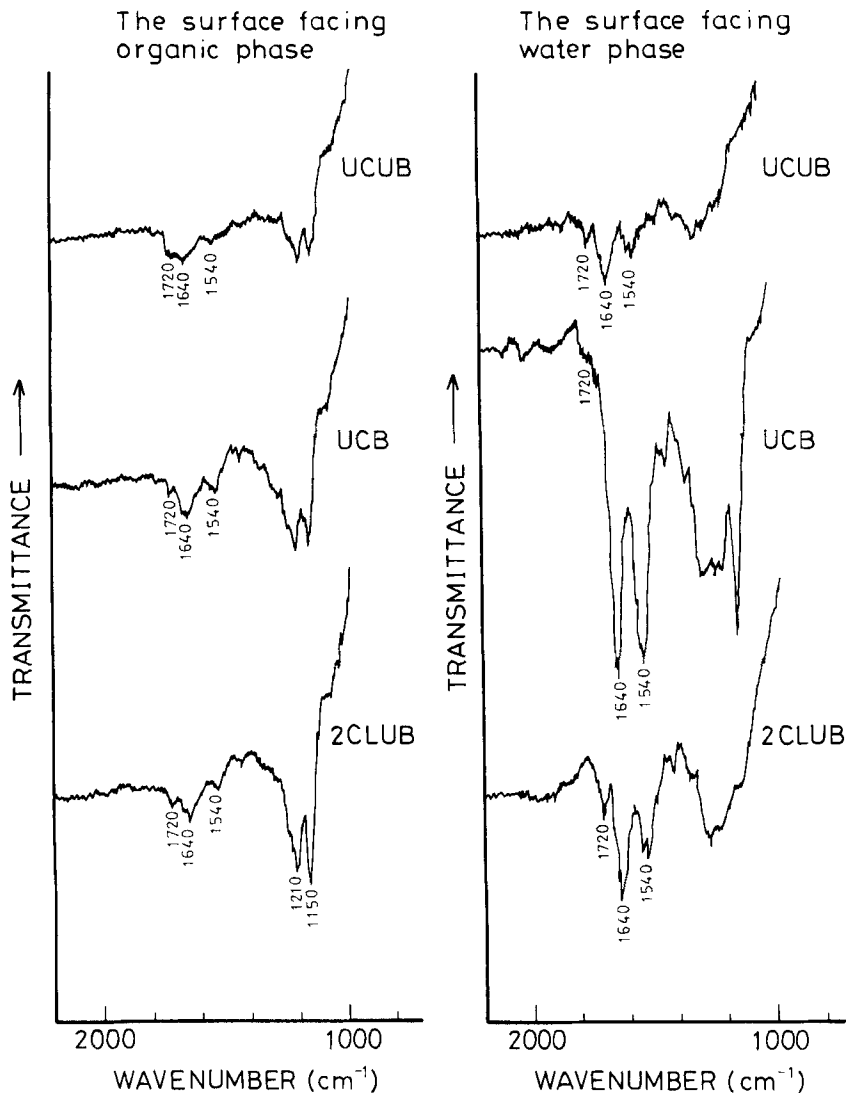As shown in Fig. 3, ESCA analysis shows similar results. The chemical structure of the face of the films adjacent to the water phase clearly

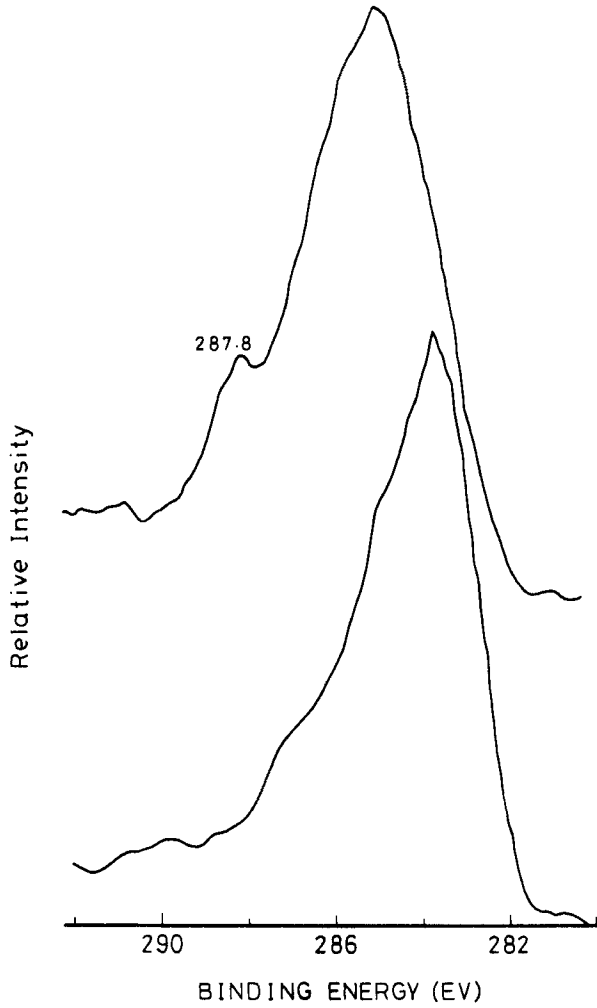FIG. 2. ATR spectra obtained from both sides of poly(BTAC-EDA) film (polymerization conditions: 25°C, 30 min).

287.8

Relative Intensity

290   286   282

BINDING ENERGY (EV)

Fig. 3. Cl_s spectra obtained from both sides of poly(BRAC–EDA) film (UCB) (polymerization condition: 25°C).

shows a stronger characteristic absorption of the amide group [13] (C1s: 287.8 eV).

During the reaction, we observed tiny bubbles being produced under the film which was dissolved in the water phase. These bubbles were produced on the surface of the film on the organic phase side, and the indicated PH was about 2–3. Therefore, the bubbles were possibly hydrochloride vapor produced by the interfacial reaction.

Effect of Alkali in the BTAC–EDA System

When sodium carbonate was added to the reaction system, the chemical structure of the surface of the films adjacent to the water phase (see Fig. 4) showed the apparent characteristic absorption of the amide group during the initial or later stages (30 min) of the reaction. Moreover, the chemical structure of the film faces adjacent to the water phase during the minute after the reaction began (see Fig. 4) are different in chemical structure from the film faces adjacent to the organic phase during the later reaction stage [see Fig. 2 (UCB)]. The latter show the characteristic absorption of the acid group. Therefore, it is certain that the film was growing toward the organic phase from the interfacial region. Therefore, the reaction region was in the organic phase.

The two faces of the film were different in chemical structure, as mentioned above. The reason for the different chemical structures on the two sides of the film is because of the characteristic features of this interfacial condensation. The main characteristic features of this interfacial condensation are that the hydrochloride produced by the interfacial reaction is neutralized almost completely by sodium carbonate during the initial reaction stage; that the reactivity and solubility of the diamine are greater than those of water; that sodium carbonate aqueous solutions do not dissolve in dichloromethane, so they cannot restrict the hydrolysis of BTAC at the later reaction stages; and that hydrolysis of BTAC is restrained, and amidation of BTAC is the primary reaction at the initial reaction stage.

As shown in Table 2, when we observe the intensity of the functional group of the amide (NH) at 1540 cm^{-1} versus that of the aromatic (C=C) at 1150 cm^{-1} [14], the amide groups increase gradually versus time. This is due to the fact that the EDA slowly dissolves in the organic phase and reacts with BTAC. Thus, the intensity ratio is small at the initial reaction stage. Hence, the reaction is a diffusion-controlled.

Before the later period of the reaction, the film is formed by the
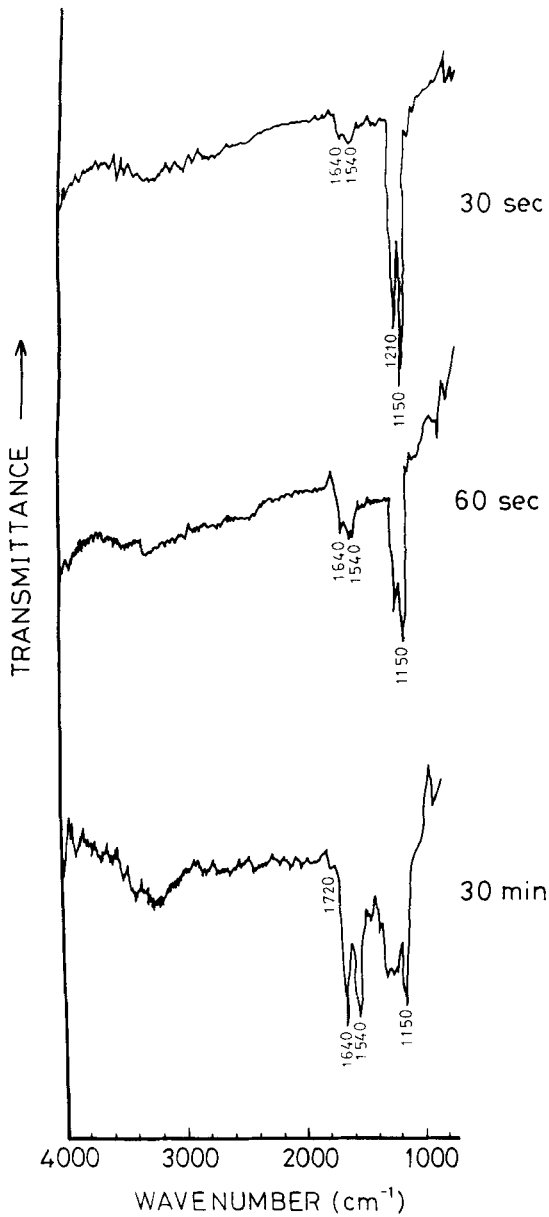
FIG. 4. ATR spectra obtained from the surface facing the water phase versus the reaction time for poly(BTAC–EDA) film (UCB).

TABLE 2. Intensity Ratio from ATR Spectra of Poly(BTAC-EDA) Films versus Reaction Time

Sample	Time, s	Intensity ratio: Amide band at 1540 cm^{-1} Aromatic band at 1150 cm^{-1}
BTAC-EDA(UCB)[a]	30	0.107
	60	0.382
	1800	1.060
BTAC-EDA(2 CLUB)[b]	30	2.130
	60	2.390
	1800	0.304
BTAC-EDA(2 CLUB)[c]	30	2.401

[a]The surface facing the water phase for poly(BTAC-EDA) film (UCB).
[b]The surface facing the organic phase for poly(BTAC-EDA) film (2 CLUB).
[c]The surface facing the water phase for poly(BTAC-EDA) film (2 CLUB).

interfacial polycondensation reaction. The hydrochloride produced by the reaction must be dissolved into the water phase and diffused out. Due to the hindrance of the film, this procedure slows down, creating a pile-up of the hydrochloride in the organic phase adjacent to the film and causing a partial acidification layer. The film itself contains a lot of acid and amide groups, and these groups can form hydrogen bonds with the water. In addition, the hydrochloride present is able to promote the hydrolysis of BTAC. Because the interface reaction is diffusion-controlled, the concentration of EDA on the interface is very low during the later stages of the reaction. Therefore, there is an apparent characteristic absorption of the acid group during the later reaction stage. A typical reaction is shown in Scheme II.

Effects of the Catalyst in the BTAC-EDA System

When TBAC is added as a phase transfer catalyst, it is observed that amidation of the film increases (see Fig. 2). And, as shown in Fig. 5, when TBAC is added, the rate of reaction during the initial reaction stage increases rapidly. This increase is due mainly to amidation. TBAC assists transfer of EDA from the water phase to the organic phase, making the rate of reaction increase. Thus, the reaction is diffusion-

$CO_3^{2-}+H_2O \rightleftharpoons HCO_3^{1-}+OH^{1-}$

$OH^{1-}+H_3O^{1+} \rightarrow 2H_2O$

CO_3^{2-}

hydrogen bond

HCl

H_2O

CH_2CCl_2

interface

$R = -CH_2CH_2-$

$H_2N-R-NH_2$

interface
film

H_2O HCO_3^{1-}

HCl   HCl

HCl

$H_2N-R-NH_3^{1+}Cl^{1-}$ H_3O^{1+}

NH_2-R-NH_2

$Cl-C \qquad C-Cl$

at initial
stage

at final
stage

SCHEME II.
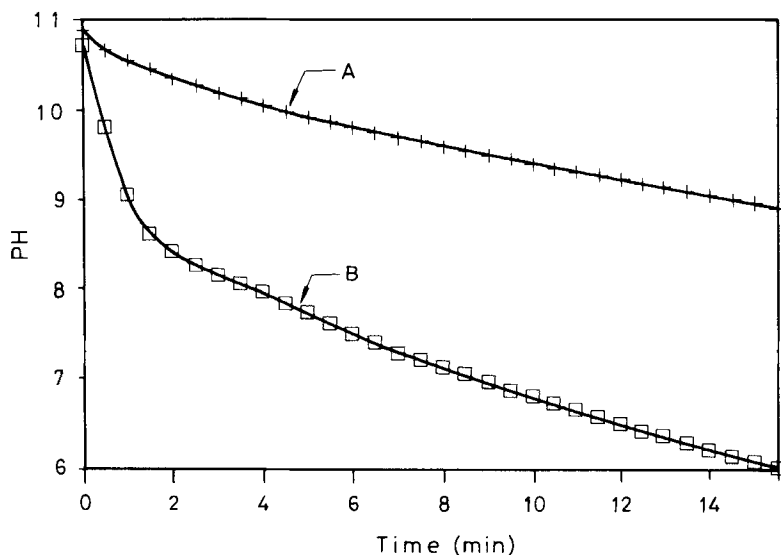
FIG. 5. Effect of catalyst on the rate of interfacial reaction (polymerization conditions: 25°C, [BTAC] = EDA] = 0.061 M). A: UCUB. B: 2 CLUB.

controlled. As shown in Fig. 6, the chemical structure of the face adjacent to the organic phase of the film shows no apparent hydrolysis reaction during the initial reaction stage, but the characteristic absorption of the acid group is apparent at the end of the reaction. The chemical structure of the film face adjacent to the organic phase during the initial reaction stage is similar in chemical structure to the film face adjacent to the water phase during the later reaction stage (30 min). Therefore, it is clear that the film is growing toward the organic phase from the interface region until the reaction is over. Thus, the reaction region of this system is in the organic phase.

Referring to Table 2, we can see that the extent of amidation when TBAC is added for forming the film face adjacent to the water phase is greater than the extent of amidation when sodium carbonate is added during the first minute of the reaction. This increase is due to TBAC assisting the transfer of EDA.

As shown in Fig. 6 (30, 60 s), the characteristic absorption splits around 3230 cm^{-1} [NH, IR(ATR) cm^{-1}: 3200, 3260], which is deemed as being partially caused by the amine groups [15]. The amine groups
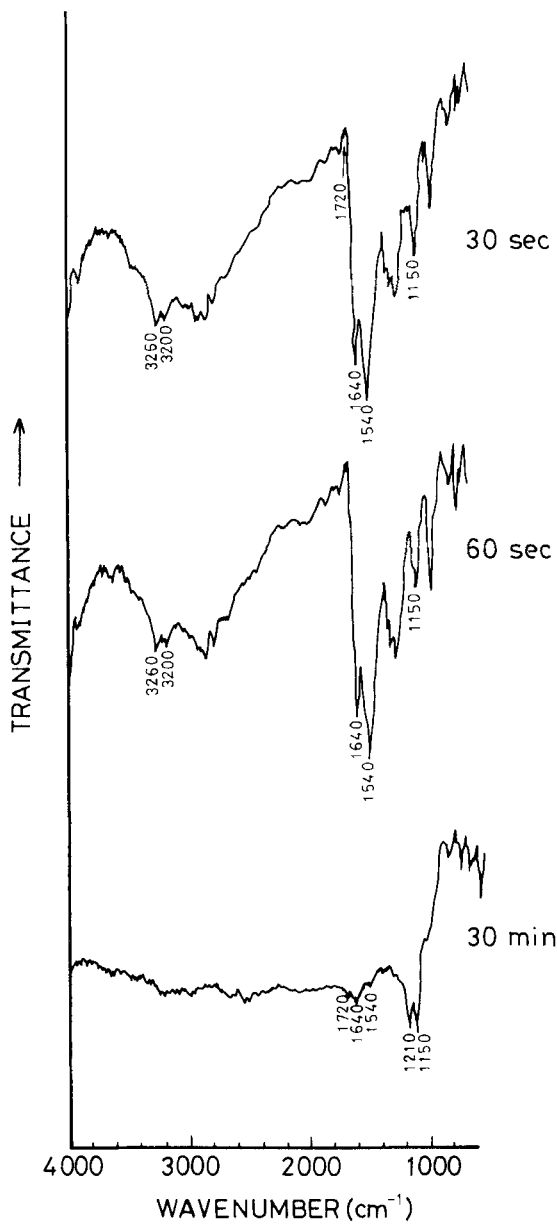
FIG. 6. ATR spectra obtained from the surface facing the organic phase versus the reaction time for poly(BTAC–EDA) film (2 CLUB).

come from incompletely reacted EDA. The transfer of EDA is assisted by TBAC, while BTAC transfers at a normal speed. Therefore, there is a lack of BTAC at the reaction region during the initial reaction stage, resulting in amine groups on the film. Therefore, the reaction is diffusion-controlled. At the later reaction stage (30 min), the characteristic absorption of the acid group is also apparent due to the same reasons given for the above sodium carbonate system. The typical reaction process is shown in Scheme III.
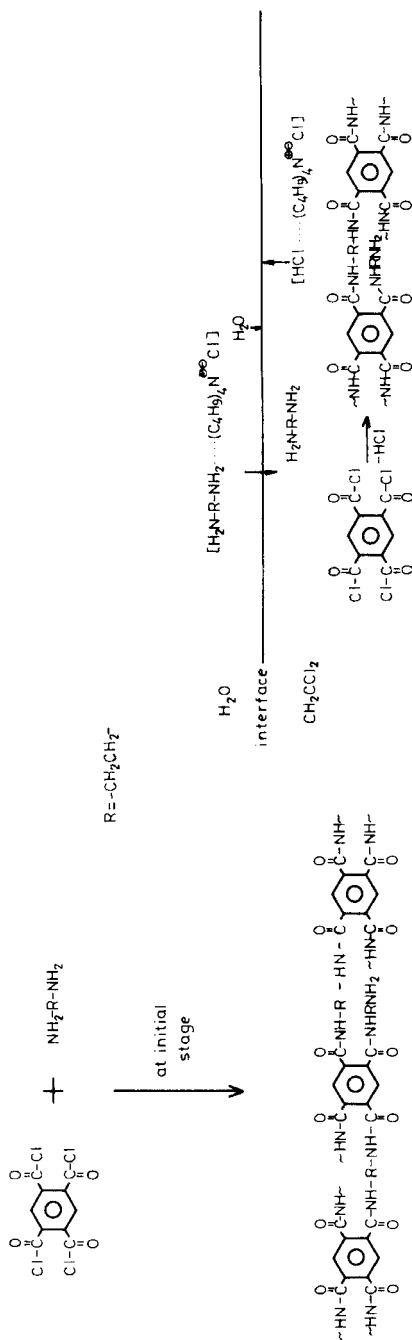
In the BTAC–EDA System without Addition of Alkali and Catalyst

Even though EDA is stronger in reactivity for nucleophilic acyl substitution than water, there is also the hydrochloride produced by the interface reaction reacting easily with EDA to form EDA hydrochloride salt. EDA hydrochloride salt is weaker in reactivity for nucleophilic acyl substitution than plain EDA. Meanwhile, the hydrochloride also catalyzes hydrolysis of BTAC. Therefore, the characteristic absorption of the acid group is apparent at the initial reaction stage. Due to the lack of alkali or catalyst, the BTAC–EDA (UCUB) system show fewer differences in chemical structures of both sides than the BTAC–EDA (UCB or 2CLUB) system (shown in Fig. 2). A typical reaction process is shown in Scheme IV.

The BTAC–MDA System

Figure 7 shows results similar to those mentioned above. In the case of addition of TBAC or sodium carbonate, the chemical structure of the film obtained on the face adjacent to the water phase shows more characteristic absorption of the amide group, while the chemical structure of the film on the face adjacent to the organic phase apparently shows characteristic absorption of the acid group. By referring to Fig. 8 we observe that when TBAC is added to form the film, the reaction rate is obviously increased at the initial reaction stage. This is also due to TBAC assisting in transferring MDA to the organic phase from the water phase.

In Fig. 9 we can see that the mean hydrolysis percentage [2] increases with reaction time. In comparison with the results in Fig. 7, note that the reaction occurs in the organic phase. In addition, the film grows toward the organic phase from the region of the interface.
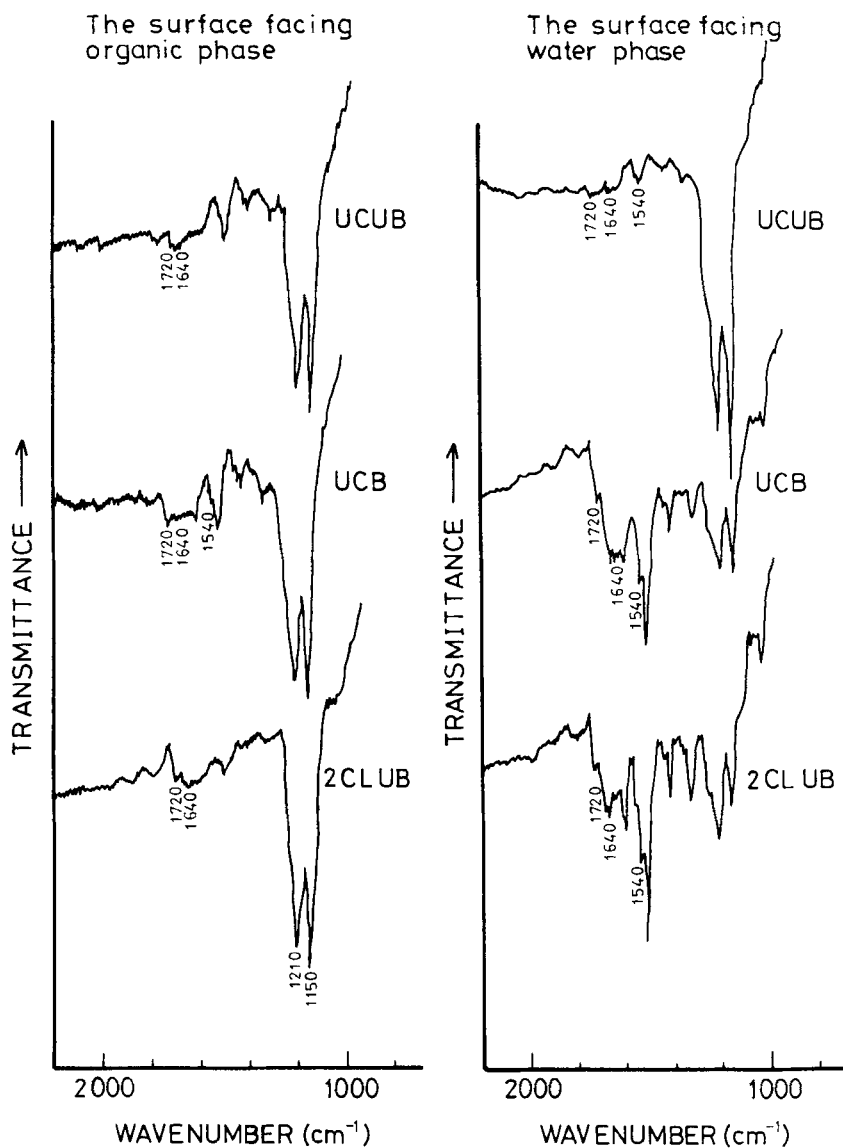
SCHEME III.

SCHEME IV.

Relationship between TBAC and Diamine

The MDA and TBAC System

^{1}H-NMR analysis showed results similar to the system to which only TBAC and hydrochloride had been added. Referring to Fig. 10 and Table 3, it is observed that the chemical shift for each hydrogen shows an apparent change. This is possible due to the linkage of TBAC and MDA. Their linkage is not damaged even in the presence of HCl. It was also observed that the presence of TBAC did not result in the MDA hydrochloride salt converting back into MDA.

The EDA and TBAC System

Figure 11 and Table 4 show that there is a change in the chemical shift for each hydrogen, indicating interaction between EDA and BTAC. However, the mode of linkage is not known.

CONCLUSION

We have presented a typical reaction process of interfacial polyfunctional condensation in our research. We came to the conclusions that:

The surface facing
organic phase

The surface facing
water phase

UCUB

UCB

2CLUB

UCUB

UCB

2CLUB

FIG. 7. ATR spectra obtained from both sides of poly(BTAC–MDA) film
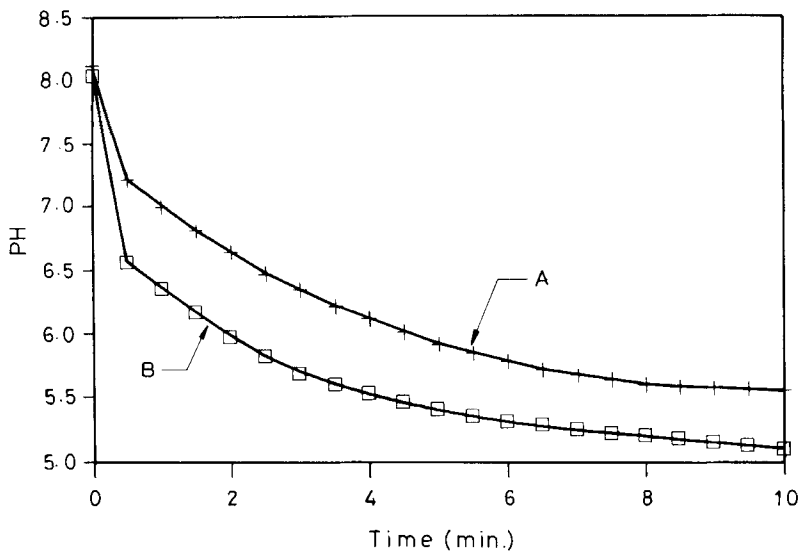(polymerization conditions: 25°C, 30 min).

FIG. 8. Effect of catalyst on the rate of interfacial reaction (polymerization conditions: 25°C, [BTAC] = [MDA] = 0.00504 M). A: UCUB. B: 2 CLUB.
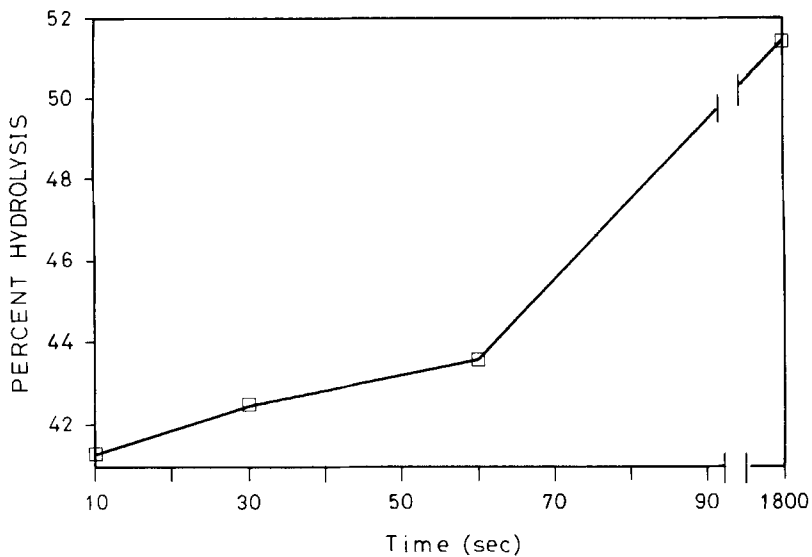

FIG. 9. Percentage of hydrolysis versus time for poly(BTAC–MDA) film (polymerization conditions: 25°C, [BTAC] = [MDA] = 0.00504 M).
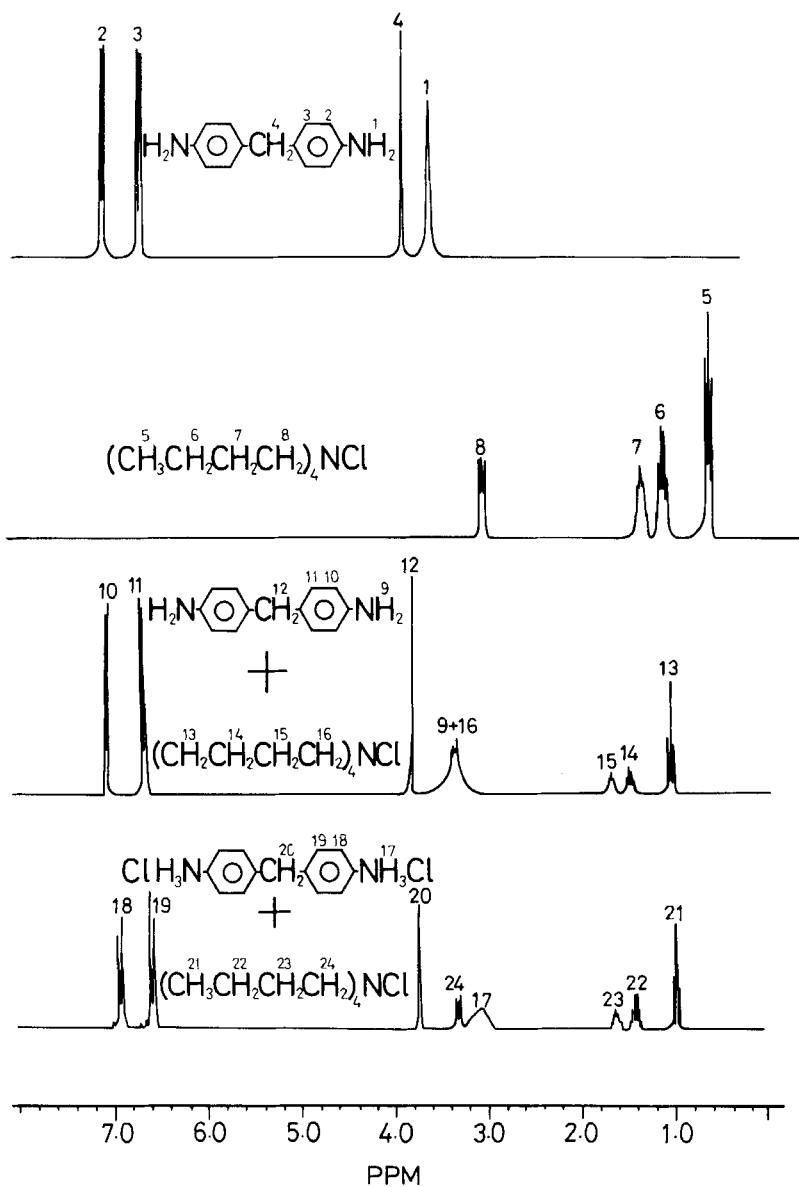
FIG. 10. ^{1}H-NMR spectra of MDA and TBAC dissolved in CDCl$_3$.

TABLE 3. Assignment of the ^{1}H-NMR Spectra of MDA and TBAC

Peak number	Chemical shift δ, ppm	Peak number	Chemical shift δ, ppm	Peak number	Chemical shift δ, ppm
1	3.52	9	3.27	17	3.07
2	7.02	10	6.94	18	6.91
3	6.63	11	6.59	19	6.59
4	3.82	12	3.75	20	3.73
5	0.58	13	0.98	21	0.97
6	1.03	14	1.40	22	1.41
7	1.26	15	1.61	23	1.64
8	2.94	16	3.27	24	3.32

(1) The interfacial polycondensation reaction region in this system is the organic phase, and the reaction is diffusion-controlled.

(2) Film formation starts from the interface and grows toward the organic phase.

(3) The film shows great differences in chemical structure on both faces when TBAC or sodium carbonate is present. More amidation is observed on the face of the film adjacent to the water phase.

(4) When sodium carbonate is added, the hydrochloride produced by the interfacial reaction is neutralized almost completely by the sodium carbonate during the initial reaction stage. Therefore, the chemical structures on the two sides of the film show great differences.

(5) Because TBAC assists the transfer of diamine, the chemical structures of both sides of the film show an apparent difference.

(6) Once TBAC links with diamine, even the presence of hydrochloride cannot damage the linkage.
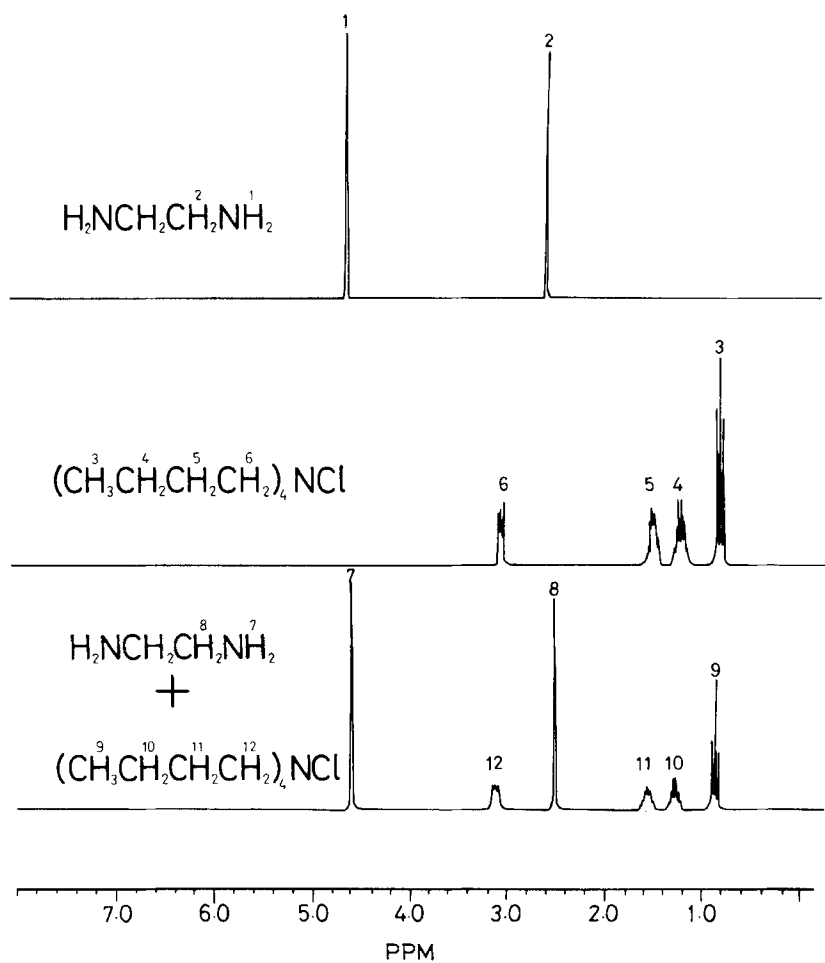
FIG. 11. ^{1}H-NMR spectra of EDA and TBAC dissolved in D_2O.

TABLE 4. Assignment of the ^{1}H-NMR Spectra of EDA and TBAC

Peak number	Chemical shift δ, ppm	Peak number	Chemical shift δ, ppm
1	4.64	7	4.63
2	2.56	8	2.55
3	0.78	9	0.87
4	1.20	10	1.28
5	1.49	11	1.58
6	3.04	12	3.12

ACKNOWLEDGMENT

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