# Phase Reversal during Water Dispersion of Polyurethane Anionomer

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**ABSTRACT:** A series of polyurethane anionomers (PUas) was synthesized from isophorone diisocyanate, polyneopentanediol adipate (P756), and hydrophilic dimethanol propionic acid (DMPA). The variation of electric conductivity and viscosity of such anionomers during water dispersion was followed. The results showed that the average diameter and polyindex of particles were reduced, the viscosity of dispersion was lowered, the time necessary for phase reversal became shorter, if the amount of DMPA or the temperature, at which the water dispersion was carried out, increased.

DSC test revealed that the order of hard segments was disturbed after water dispersion. IR spectra demonstrated that, after the chain extender ethyl diamine was added into the PUa dispersion, the hydrogen bonding of NH with carbonyls was stronger, if the dispersion temperature and the mass fraction of DMPA increased. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1234–1239, 2006

**Key words:** polyurethane; aniomomer; phase reversal; waterborne coating

## INTRODUCTION

Waterborne polyurethane could be prepared by adding water into segmented polyurethane ionomer containing very small amount of solvent as diluent. During addition of water, polyurethane ionomer disperses gradually into water and phase reversal takes place. The system of water in oil turns into the system of oil in water. There were some reports[1–6] about such a phase reversal process. According to these published reports, water was absorbed first on the surface of the hydrophilic hard segment microionic lattices, and only the ionic groups on the surface of the hard segment microionic lattices were dissociated.[2] After this stage, the water entered into the hydrophilic disordered hard segment microionic lattices, and then into the hydrophilic ordered hard segment microionic lattices. At last, as great amount of water was added, phase reversal was completely finished.

The present work focuses attention on the effect of the mass fraction of hydrophilic dimethanol propionic acid (DMPA) and the temperature of water dispersion on the particle size and on the morphology of the dried film of the segmented polyurethane anionomer (PUa) made from isophorone diisocyanate (IPDI), polyneopentanediol adipate (P756), and DMPA.

## EXPERIMENT

### Materials

Isophorone diisocyanate (IPDI): from the Institute of Spaceflight of China; P756: $M_n$ = 2000, functionality 2, produced by Yantai Synthetic Leather Co.; dimethanol propionic acid (DMPA): synthesized by Konda Chemical Reagent Co.; dibutyltin dilaurate (DBTDL): provided by Goldschmidt Co.; and triethylamine (TEA), *N*-methyl-1-pyrrolidone (NMP), and ethyl diamine (EDA): reagent grade, supplied by Shanghai Linfeng Chemical Reagent Co. P756 was dewatered under vacuum at 110°C for 2 h, and DMPA at 80°C for 1 h before use.

### Synthesis

IPDI and catalyst DBTDL was added into a four-necked flask equipped with a stirrer, a reflex condenser, a $N_2$ inlet and containing the mixture of 30 g of P756 with some DMPA. The mass fraction of DMPA was 4–7%, based on the total reactants, and the molar ratio of —NCO to —OH was 1.8. The reaction was carried out at 80°C for 3 h, until the theoretical content of —NCO was reached. Thereafter, 5 g of NMP was charged into the flask to lower the viscosity of the formed segmented polyurethane. TEA was then added, equivalent to the molar quantity of DMPA, for neutralization of the resultant. Deionized water (55 g) was poured under stirring (2400 rpm) into the flask at 20, 40, or 60°C. An isobaric funnel was used to keep the total period for adding water equal to 199 s. Electric conductivity and viscosity of the system was de-
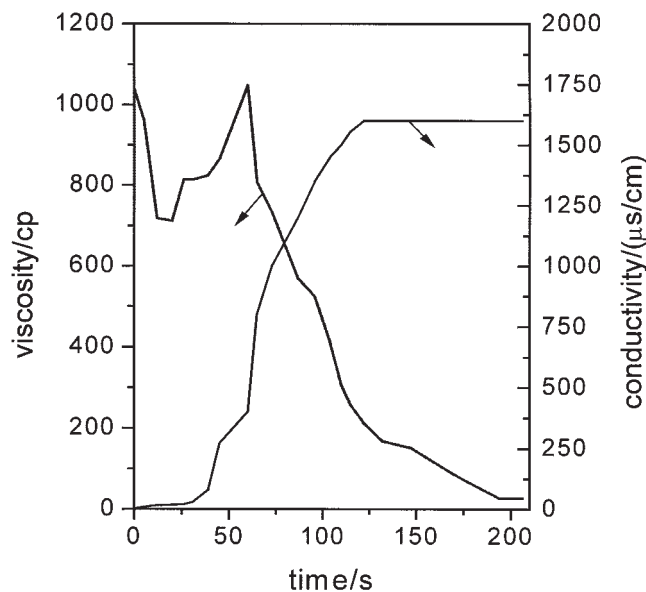
**Figure 1** Variation of conductivity and viscosity during water dispersion.

termined during the process of water dispersion. After water dispersion, a solution of the chain extender EDA in water with the concentration of 2.5% was added into the polyurethane anionomer (PUa) dispersion at 40°C, and the mass ratio of IPDI/EDA was 10 : 1. At last, the terminal —NCO groups were capped by di-ethanolamine. The solid content of the water dispersion was ~30%.

### Determination and characterization

Electronic conductivity was measured using a DDS-II D conductivity meter, available from Shanghai Leiz
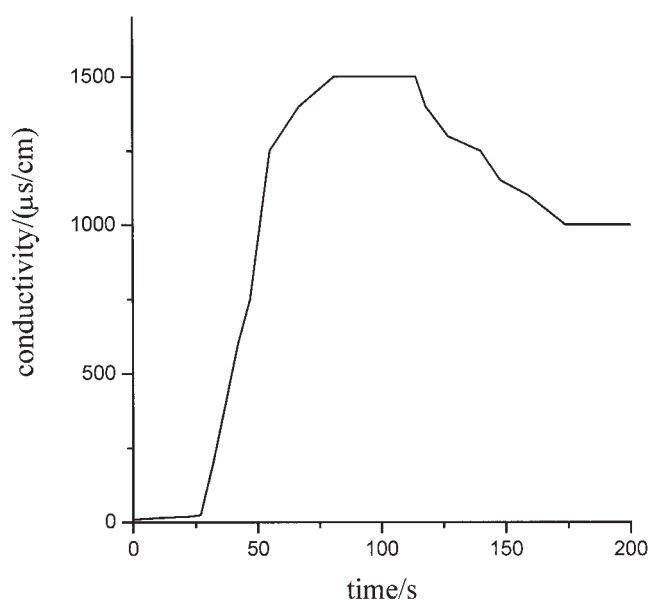


**Figure 2** Conductivity curve of the sample 6–60.

**TABLE I**
**Particle Size of Different Dispersion Samples**

| Sample | Particle size ($\mu$m) | Specific area (m$^2$/g) | Polyindex |
|--------|-----------------------|------------------------|-----------|
| 4–20 | 68.12 | 1.92 | 1.48 |
| 4–40 | 0.19 | 34.1 | 0.20 |
| 4–60 | 0.19 | 34.4 | 0.20 |
| 6–20 | 59.90 | 12.0 | 2.23 |
| 6–40 | 0.19 | 34.5 | 0.20 |
| 6–60 | 0.19 | 34.5 | 0.20 |
| 7–40 | 28.59 | 12.3 | 3.66 |
| 7–60 | 0.19 | 34.8 | 0.20 |

Instrument Co. Approximate viscosity was followed by a SZG-441c rotational speed meter manufactured by Shanghai Rotational Speed Meter Co. to determine the rotational speed of the stirrer, and the rotational speed was then transformed to viscosity in accordance to a working curve that was drawn in terms of the relationship between the rotational speed of the stirrer and the viscosity of the mixtures of honey with different amounts of water. The particle size, specific area, and polyindex of the dispersed PUa was characterized using a MASTER 2000 photoelectron spectrometer supplied by Marlven Co. The 200PC DSC and the NICOLET 5SXC FTIR instrument were used to characterize the morphology of the PUa dry film, which was prepared by pouring the water dispersion of PUa onto a Teflon plate and dried at 60°C under vacuum for 1 week.

## RESULTS AND DISCUSSION

### Phase reversal during water dispersion

The content of DMPA, temperature of water dispersion, speed of water addition, starting rotation speed of stirrer, degree of neutralization, and type of solvent could influence the act of phase reversal. In the present work, the effect of mass fraction of DMPA and the temperature of water dispersion was investigated, while the other parameters were kept constant.

Water was poured into a series of PUa samples containing different mass fraction of DMPA at different temperature. Among them, eight dispersions containing 4–7% DMPA showed very little deposits. The code X–y is used in this paper to represent the disper-

**TABLE II**
**Viscosity of Water Dispersions**

| Sample | Viscosity (cP) |
|--------|----------------|
| 4–40 | 4.9 |
| 4–60 | 5.8 |
| 6–40 | 11.5 |
| 6–60 | 13.0 |
| 7–60 | 16.5 |

TABLE III
Period for Phase Reversal

| Sample | Period for phase reversal (s) |
| --- | --- |
| 4–40 | 132 |
| 4–60 | 82 |
| 6–40 | 117 |
| 6–60 | 73 |
| 7–60 | 64 |

sion. The letter $X$ denotes the mass fraction of DMPA (%) and $y$ the temperate at which water dispersion was carried out.

Figure 1 shows typical curves of variation of electric conductivity and viscosity during water dispersion (sample 7–60). It reveals that the process of water dispersion could be approximately divided into four stages. In the first stage, the conductivity increased only a little, and the viscosity dropped, when water was adsorbed on the surface of the hard segment microionic lattices. In the second stage, the conductivity was raised sharply, meaning that water entered easily into the interior of hydrophilic disordered hard segment microionic lattices, because the hydrogen bonding between the disordered hard segments was very week, and the accumulation of such hard segments was loose. In the second stage, the viscosity became higher because of the aggregation of hydrophobic soft segments (P756), resulted from the moving of NMP, which was both hydrophobic and hydrophilic, from the solvation sheath around soft segments into the water phase. In the third stage, water entered into the interior of ordered hard segment microionic lattices.
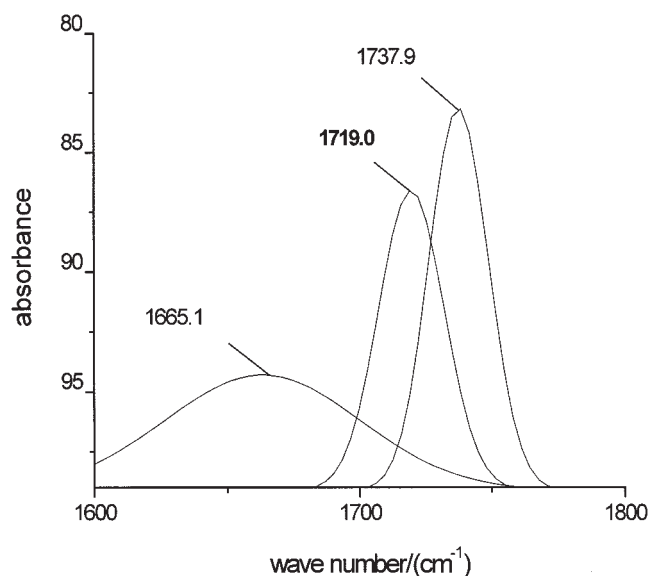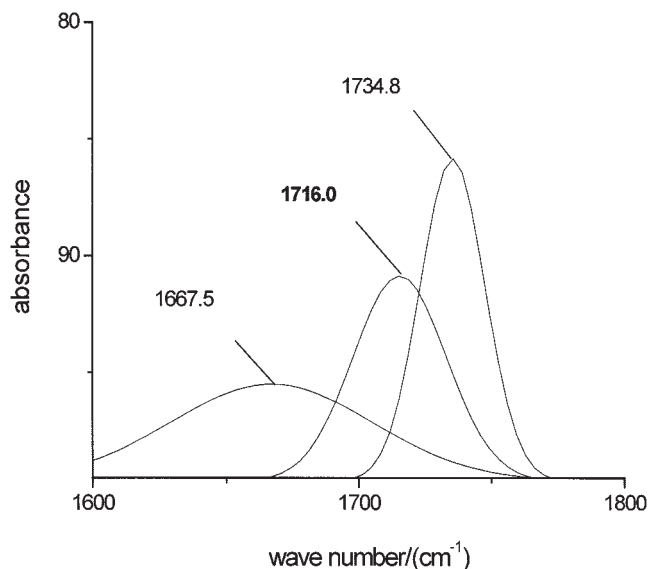


**Figure 4** FTIR spectra of the dry film obtained at the 60th second.

The hydrogen bonding between the ordered hard segments was stronger than that between the disordered hard segments, and the accumulation of ordered hard segments was so compact that the entering of water became difficult. This should be the reason why the slope of the conductivity curve reduced in this stage. The viscosity in the third stage reached the maximum because more and more NMP moved over to the water phase, and the hydrophobic soft segments lost the solvation sheath almost completely, and aggregated tighter. The phase reversal began when the dispersion became turbid. In the last stage, the conductivity reached its maxi-
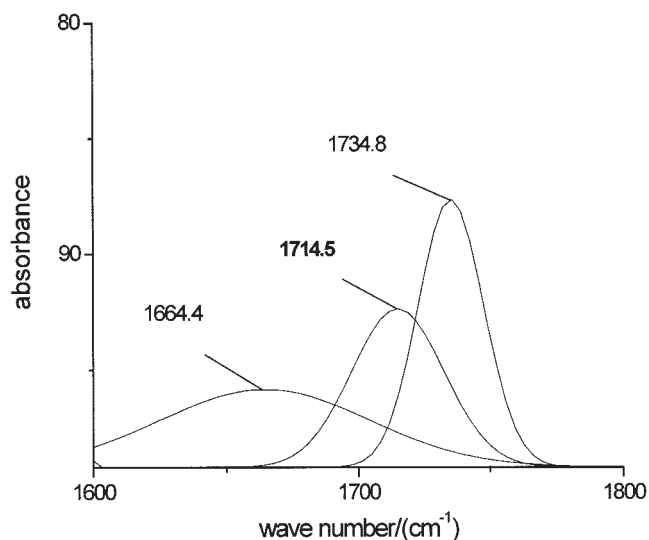


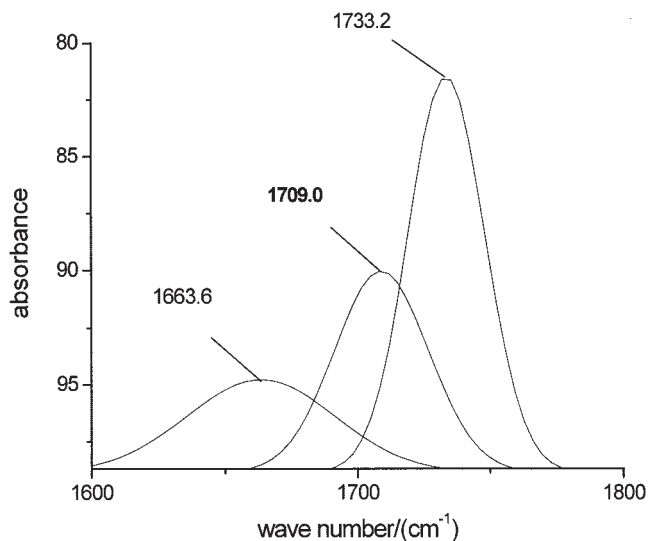**Figure 3** FTIR spectra of the dry film obtained at the 20th second.



**Figure 5** FTIR spectra of the dry film obtained at the 100th second.

**Figure 6** FTIR spectra of the dry film obtained at the 180th second.



**Figure 8** DSC Spectra of different dry films ([#], after chain extension with EDA).

mum, remained constant, and the viscosity reduced sharply, because large amount of water entered. (Owing to the problem of lower sensitivity of the conductivity meter, the conductivity curve is tardy in Fig. 1.)

The above process indicates the typical course of phase reversal of PUa made from IPDI, P756, and DMPA. There was, however, exception sometimes. As Figure 2 shows (sample 6–60), the conductivity could drop after it reached the maximum. This drop might be attributed to the possibility that some counter ions outside the electrical double layer were adsorbed by the dispersed PUa particles again.
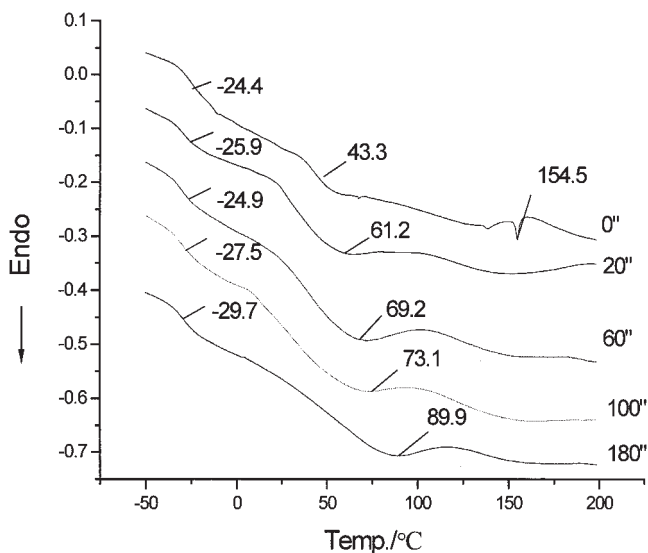
## Size and polyindex of particles

As seen in Table I, higher dispersion temperature results to smaller average particle size (greater specific area) and lower value of polyindex at the same mass fraction of DMPA. Smaller value of polyindex means narrower distribution of particle size. In the light of the Kelvin equation about the dissolution equilibrium for solid in liquid, small particles would aggregate with large particles, causing instability of dispersion. For this reason, the dispersion with the smallest value of polyindex (0.20) in Table I had the best storage stability of more than 12 months and the smallest average particle size (0.19 $\mu$m). This proves the very important effect of the temperature of phase reversal on the quality of the water dispersion.
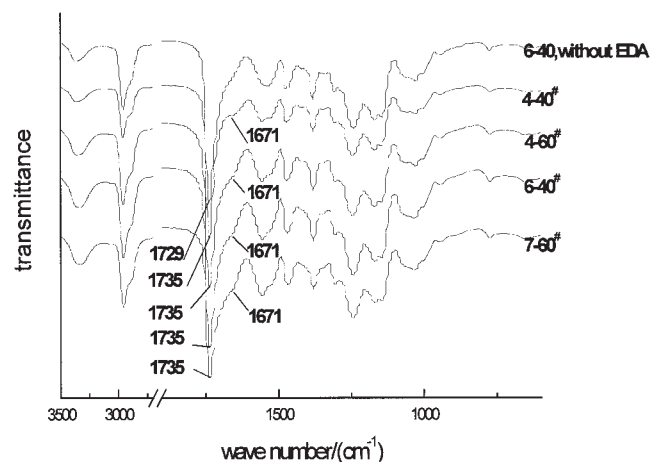


**Figure 7** DSC spectra of the dry film (7–60) prepared at different time.



**Figure 9** FTIR spectra of different films ([#], after chain extension with EDA).
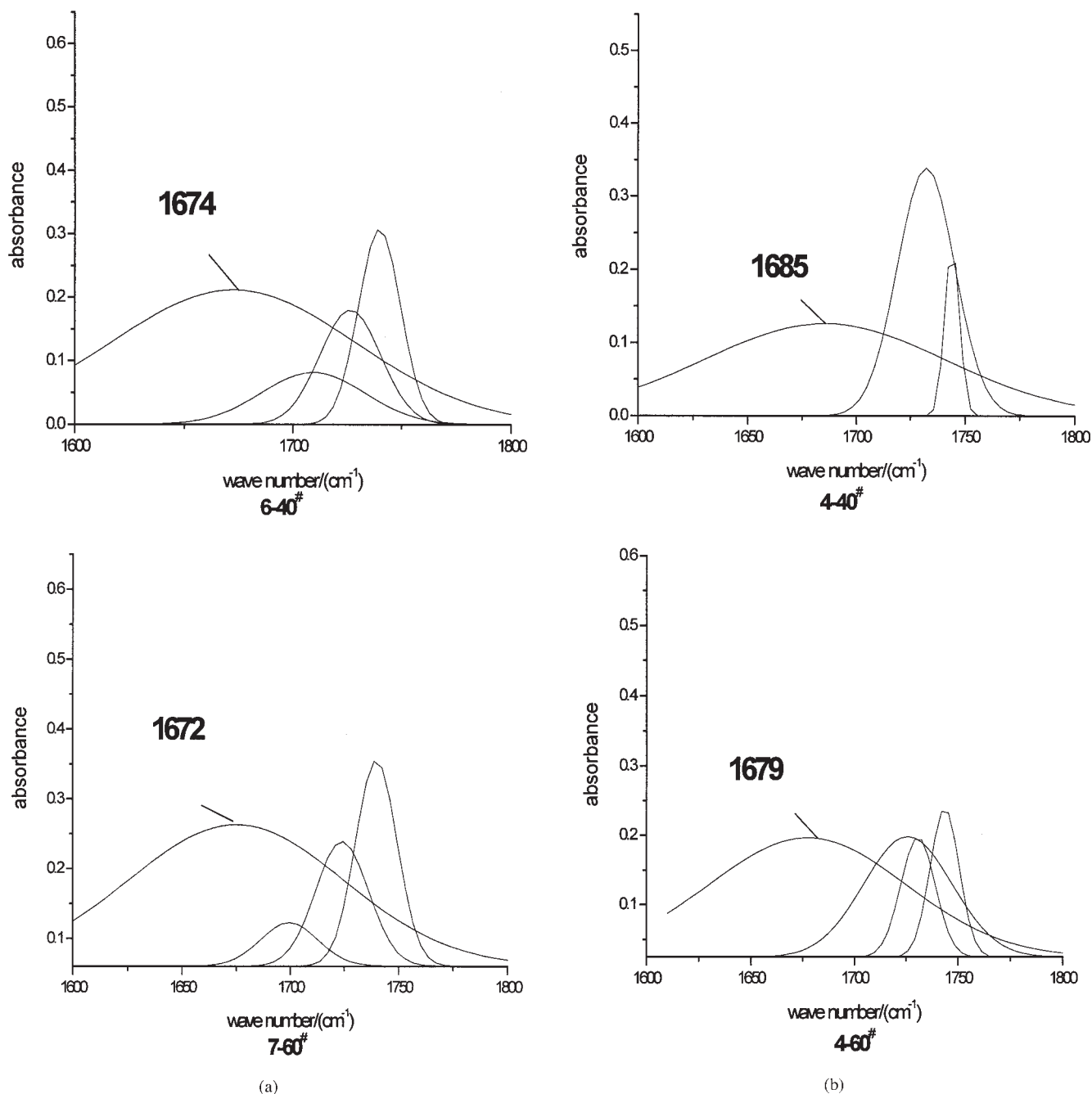
**Figure 10**  Characteristic peaks of urea carbonyl group of different dry films obtained after chain extension.

**Viscosity of water dispersion**

The final viscosities of the five most stable dispersions are listed in Table II. It could be concluded thereby that smaller particle size (see "specific area" in Table I) led to higher viscosity, which was in keeping with the principle of electrical double layer.

**Velocity of phase reversal**

The period for phase reversal in Table III means the time from addition of water to sharp drop of viscosity. Higher

temperature of water dispersion needed shorter time for completion of phase reversal, if the mass fraction of hydrophilic monomer was constant. Higher mass fraction of hydrophilic monomer also resulted to shorter period of phase reversal at constant temperature. It could be concluded that higher speed, at which the water entered into the hard segment microionic lattices, could bring about higher speed of aggregation of hydrophobic soft segments. Combining the values in Table III and I, it is clear that faster phase reversal should be helpful for the formation of smaller and uniform particles.

## Morphology of dry film obtained during water dispersion process

Figure 3–6 are the FTIR spectra of the urethane C=O of the PUa dry films prepared at the 20th (Stage 1), 60th (Stage 2), 100th (Stage 3), and the 180th (Stage 4) second during water dispersion process. It could be seen that the absorption peak of hydrogen bonded urethane C=O shifts toward lower wave number (1719–1716–1715–1709 cm$^{-1}$) along with longer time. It should imply that hydrogen bonding energy was enhanced. This might be in relation to the hydrophilic COOH groups attached to the hard segments. In the earlier stage of water dispersion, some COOH groups embedded in the coils of the macromolecular chains were not neutralized completely and form weak hydrogen bonds with urethane groups. With the entry of more and more water into the system, these hydrophilic COOH groups trended to "leave the bulk" of PUa, and moved toward water phase, which led to breaking the hydrogen bonds between COOH and urethane groups, and formation of more stronger hydrogen bonds between NH and C=O groups of urethane.

From Figure 7, it could be seen that the dissociation temperature of the short-range order of hard segments increases from Stage 1 to Stage 4 (20–60–100–180), which is identical with the variation of the hydrogen bond energy.

## Morphology of dry films obtained after water dispersion and chain extension with EDA

Figure 8 shows that three transition temperatures exist before water dispersion of the dry film 6–40: glass transition of soft segments at $-28.2°C$, dissociation of short-range order of hard segments at $54.9°C$, and dissociation of longer range order of hard segments at $155.5°C$. After water dispersion, there is only one peak at $88.9°C$, meaning the ordered region existing in hard domain was disturbed by water. The vitrification temperature of soft segments increases from $-28.7$ to $-27.9°C$, which means that the degree of microphase separation decreased after water dispersion.

The curves $4–40^{\#}$, $4–60^{\#}$, $6–40^{\#}$, and $7–60^{\#}$ in Figure 8 are the thermograms of the dry films obtained after chain extension with EDA of the corresponding phase reversed PUa dispersion. It could be found that the temperature of the dissociation of short-range ordered hard segments increased after chain extension (see the sample $6–40^{\#}$ in Fig. 8). This should be ascribed to the

urea groups resulted from the reaction of EDA with —NCO. Stronger hydrogen bonds could form between urea groups. Figure 9 discloses that the FTIR spectrum of the dry film 6–40 without EDA shows the characteristic peak of urethane C=O at 1729 cm$^{-1}$, whereas the other not only this peak but also the peak of urea C=O at about 1671 cm$^{-1}$.[7–8]

In the range from 1735 to about 1671 cm$^{-1}$, multiple bands could be observed. After separating these peaks, Figure 10 was obtained. According to Figure 10, the characteristic band of urea C=O group shifts also toward lower wave number by increasing the mass fraction of DMPA and the temperature of water dispersion. The phenomenon was related to formation of stronger hydrogen bonds between urethane and urea, and between urea groups. More mass fraction of DMPA and higher phase reversal temperature made positive contribution to the transference of COOH groups to the water phase, which was beneficial for the formation of stronger hydrogen bonds between urethane and urea[9] as well as between urea groups.

## CONCLUSIONS

More mass fraction of DMPA and higher temperature during water addition led to faster phase reversal, smaller particles, lower value of polyindex, and higher viscosity of the water dispersion of PUa based on IPDI, P756, and DMPA. Stable waterborne PUa could thus have been obtained. Stronger hydrogen bonds were formed between urethane and urea as well as between urea and urea after chain extension of such PUa dispersion with EDA, if the temperature of phase reversal and the mass fraction of DMPA were higher.

### References

1. Chen, S.-A.; Chan, W.-C. J Polym Sci Part B: Polym Phys 1990, 23, 352.
2. Chen, S.-A.; Chan, W.-C. J Polym Sci Part B: Polym Phys 1990, 23, 1515.
3. Von.O. Lorenz, F.; Haulena, D. Kleborn. Zum. Kautschukelastischen Verhalten von Plyurethane -Ionomeren. Die Angewandte Makromoleculare Chemie 1973, 33, 159.
4. Otto Lorenz, H. Ein von Loesungsmitteln auf den Particledurchmesser von Dispersionen anionischer Polyurethanionomerer. Die Angewandte Macromoleculare Chemie 1978, 72, 115.
5. Lu, X.-S.; Hao, G.-J.; Guo, T.-Y.; Song, M.-D.; Zhang, B.-H. Acta Polymerica Sinica 2001, 3, 320.
6. Jun, G. Beijing Building Material 1997, 2, 16.
7. Xiu, Y.-Y.; Zhang, Z. P.; Wang, D.; Ying, S.-K. Polym Rep 1992, 3, 1335.
8. Luo N.; Pang, Z.-Q.; Wang, D.; Ying, S.-K. Polym Sci B 1994, 36, 828.
9. Luo, N.; Wang, D.-N.; Ying, S.-K. Polymer 1996, 37, 3045.