

카르복실화된 폴리카프로락톤에 의한 수분산 폴리우레탄의 제조와 특성(I)

양정은, 곽용실, 박상우, 이동진, 김한도
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Preparation and Properties of Aqueous Dispersions of Polyurethane Anionomers Based on Carboxylated Polycaprolactone(I)

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1. INTRODUCTION

Ionomers contain a certain number (usually 10mol% or less) of inorganic salt groups attached to a polymer chain.¹⁻⁴ Ionization has a strong effect on many of their physical properties. Even small amounts of ionic groups can sufficiently modify specific properties of materials.

Because of interionic electrostatic forces, as well as the incompatibility between the ionic groups and the nonpolar polymer matrix, the ionic groups tend to aggregate. In general, above a critical ion concentration, two types of ionic aggregates can be defined: multiplets and clusters.^{1,2} The multiplets are small associated polar groups, and the clusters are significantly larger aggregations of multiplets with weaker ionic interaction.

From a processing standpoint, it would be highly desirable if the aggregates could be made to dissociate at processing temperatures and reform at use temperature, because the persistence of the ionic aggregates to high temperatures leads to melt viscosities that can be orders of magnitude greater than the analogous nonionic polymers. Although the dissociation of ionic aggregates could be dissociated when the polymer matrix and ionic structure were changed.

Further improving the compatibility between the ionic groups and the polymer matrix as well as changing the ionic type may destroy or weaken the ionic aggregation. Then the salt groups might be distributed in the polymer matrix in the form of ion pairs or multiplets, and no clusters would exist. Polycaprolactone (PCL) is known for its good compatibility, and carboxylate is advantageous to ionic aggregate dissociation.

In this study, the carboxylate group was introduced into the PCL soft segment, and

based on this, a new family of aqueous dispersions of polyurethane anionomers was prepared. The microstructure and properties of those ionomers were studied by different techniques.

2. EXPERIMENTAL

2.1. Materials

Monomer ϵ -Caprolactone (CL, Aldrich) was dried over calcium hydride at room temperature for 24h, then distilled under reduced pressure before use. Dimethylol propionic acid (DMPA, Aldrich) and dimethylol butanoic acid (DMBA, Aldrich) were dried in a vacuum oven (100°C) for at least 5h. 4, 4'-Diphenylmethane diisocyanate (MDI, Aldrich) was used without further purification. Di-n-butyltin (IV) dilaurate (DBTDL) and stannous octoate (Aldrich) were used as a catalyst. Ethylenediamine (EDA, Kasei, Japan) and acetone were dried over 4Å molecular sieves before use. Triethylamine, ammonia water, cupric hydroxide, and cupric acetate as a neutralization were used.

2.2. Synthesis

The reaction proceeded under nitrogen protection in a four-necked flask equipped with a reflux condenser, a gas inlet, thermometer, and a stirrer. Caprolactone was mixed with the stoichiometric amount of DMPA (or DMBA). After reaction at 80°C for 24h, the products were vacuum distilled to remove the unreacted CL, then washed with water to remove the DMPA (or DMBA). The products were dried in a vacuum oven at 80°C for a week. The reaction procedure is outlined in Figure 1. The oligomers were characterized by titration and DSC measurement.

A 3 : 2 : 1 MDI : EDA : CPCL (or DPCL) segmented polycaprolactone-polyurethane used as the control polymer in this study was synthesized by a typical two-step condensation reaction. The series of aqueous dispersions of polyurethane anionomers with different composition were synthesized as follows. CPCL (or DPCL) and MDI/acetone were placed in the flask with stirring. The reaction was carried out at about 80°C under dry nitrogen until the NCO group content reached a given value that was calculated based on that all the hydroxy groups were consumed by NCO groups, as determined by the di-n-butylamine titration method. Chain extension and distilled water were carried out dropwise to the prepolymer at 40°C for 1h with vigorous stirring. The solution was neutralized by adding a neutralization at 50°C for 30min. An aqueous dispersions of 35 wt% solid was obtained after removal of acetone by vacuuming.

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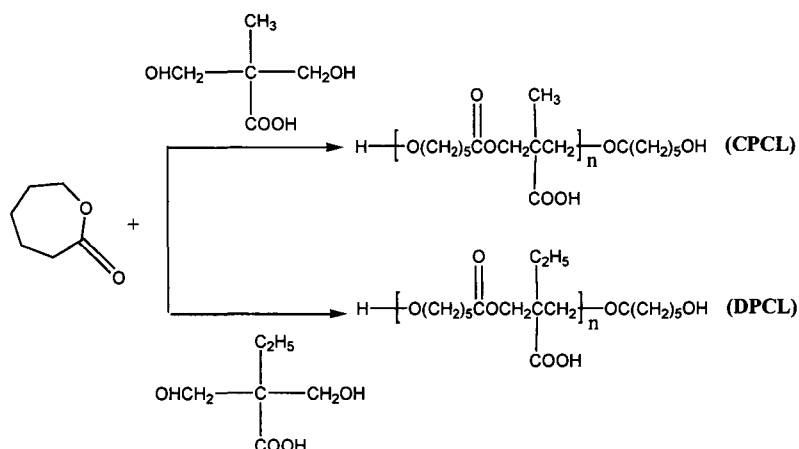


Figure 1. Synthetic route to carboxylated polycaprolactone.

Polyurethane films were cast from emulsion on a Teflon plate and dried at 70°C 3h. The remaining moisture was removed at 60°C 20mmHg for the next 24h.

2.3. Characterization

Infrared (IR) spectroscopy was performed by using a Fourier transform infrared spectrometer (Impact 400D, Nicolet). The spectra were recorded at 4cm⁻¹ resolution, and 32 scans were collected for a good signal averaging to obtain a signal-to-noise ratio.

Differential scanning calorimetry (DSC) thermograms over a temperature range of -100°C ~250°C was recorded using DSC 200C (Seiko) with a heating rate of 10°C/min.

Thermogravimetric behavior of the films over the temperature range of 50-450°C was measured using a TA thermogravimeter analyzer with a heating rate of 10°C/min under nitrogen purging.

The tensile test was carried out with a United Data System (Instron, SSTM-1) following the ASTM-D638 specifications. The cross-head speed was 20mm/min.

3. RESULTS AND DISCUSSION

It has been reported that the ring-opening polymerization of caprolactone in the presence of hydroxy carboxylic acid under lower temperature has proven that the active propagation site is only on the hydroxy terminal. We used dimethylol propionic acid or dimethylol butanoic acid as an initiator to synthesize carboxyl polycaprolactone diol.

The number-average molecular weights of CPCL and DPCL measured by hydroxyl number titration and acid value titration. The hydroxyl numbers of CPCL and DPCL were determined by a standard procedure (ASTM D 4274-method A). Fourier deconvoluted spectra for CL, DMPA, DMBA, CPCL, and DPCL are shown in Figure 2.

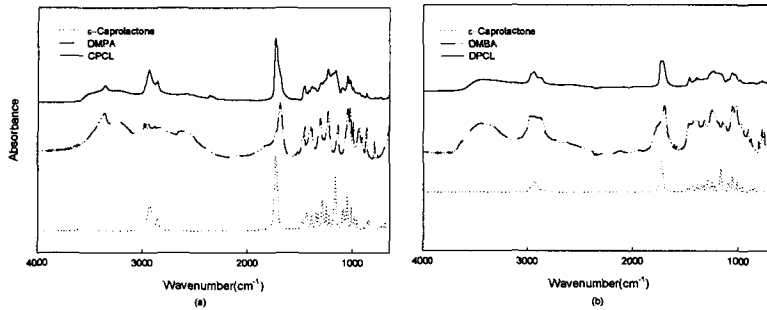


Figure 2. FTIR spectra of carboxylated polycaprolactone (a)CPCL and (b)DPCL.

Polycaprolactone containing carboxyl groups (CPCL Mn=1300, DPCL Mn=1300) were prepared from caprolactone and dimethylol propionic acid or dimethylol butanoic acid. Aqueous dispersions of polyurethane anionomers based on the polycaprolactone were synthesized from MDI, EDA.

4. REFERENCES

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