

The Polycondensation of Lithium 11-Bromoundecanoate in Aqueous Media

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ABSTRACT: To obtain a biodegradable plastic, polycondensation, the substitution of bromine by carboxylate was carried out on lithium 11-bromoundecanoate. Using water as a solvent, the formation of a double bond was detected between 70 and 100°C, yielding a good quantity of polymer. Water is recommended as the best solvent for the reaction. Thermodynamic investigations were carried out by using ethylene glycol and water. The reaction is believed to proceed according to the S_N2 mechanism. The ΔH and ΔG values for condensation in ethylene glycol were slightly higher than for those in water, but the reaction rate in water at 70°C was 7 times greater than that in ethylene glycol. The enhancement of dissociation accounts for the advantageous condensation in aqueous media. Furthermore, ΔS shows

negative values and ΔG shows positive values, meaning that the reaction should proceed exothermically and not spontaneously. Experiments to condense 11-bromoundecanoate in aqueous media were carried out for ten days in a water bath, kept at 70°C, using 25 mL of 0.05M 11-bromoundecanoate. The degree of polymerization for the resulting polymer was found to be 23 by the end group assay for both bromine and carboxylate. Neither a melting point nor glass transition point for the product were observed. The polymer formed decomposes at 300°C and instantly disperses. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 130–134, 2003

Key words: polycondensation; polyester; biodegradable; 11-bromoundecanoate; thermodynamics

INTRODUCTION

Polymers originating from living organisms may be decomposed in nature, but most polymers made of petroleum are for more resilient.

Polymers that can be biologically decomposed are called biodegradable polymers or “green plastics.” They have received a great deal of attention from the viewpoint of environmental protection. Aliphatic polyesters are well-known biodegradable polymers. The crucial property of these polymers is the ability for esters to undergo hydrolysis, resulting in chain cleavage. Those polymers have found applications in the field of medicine as temporary aids for short-term biological dysfunctions.

The range of biodegradable plastics include polylactate, polybutylene succinate adipate, polycaprolactone, polyadipate-caprolactone, cellulose ester, and modified starch.^{1,2} Most biodegradable polymers mentioned above have been synthesized by polycondensation between oxycompounds and carboxylic acids, or dehydration^{3,4} and biodegradation mechanisms are investigated.⁵ Also, bulk polycondensation for a chloro-fatty acid sodium salt has been tried.⁶

To date, no published research papers have revealed an economical method for the polycondensation of 11-bromoundecanoate. Therefore, polycondensation of lithium 11-bromoundecanoate, from various solvents such as *N,N*-dimethylacetamide (DMAC), dimethylformamide (DMF), ethylene glycol, and water is investigated in this study.

EXPERIMENTAL

Initially, 10 g of 11-bromoundecanoic acid was dissolved in 100 mL of methanol. A slightly lesser amount of lithium hydroxide was then added to the methanol-11-bromoundecanoic acid solution a little at a time. Adding an appropriate amount of acetone caused lithium 11-bromoundecanoate to precipitate. Polycondensation was carried out in a 50 mL sample bottle placed in a water bath kept at the desired temperature. The degree of polymerization was calculated both by determining of the amount of bromide ion formed in the media, and by performing an assay of bromine and carboxylic acid in the end group. For the assay, a product obtained was burned in a 500 mL burning flask filled with oxygen, followed by dissolving it in an appropriate amount of water. One or two drops of hydrogen peroxide were added to the water. The amount of bromine linked to end of polymer chains was measured by titration of the solution using a 0.01M silver nitrate standard solution.

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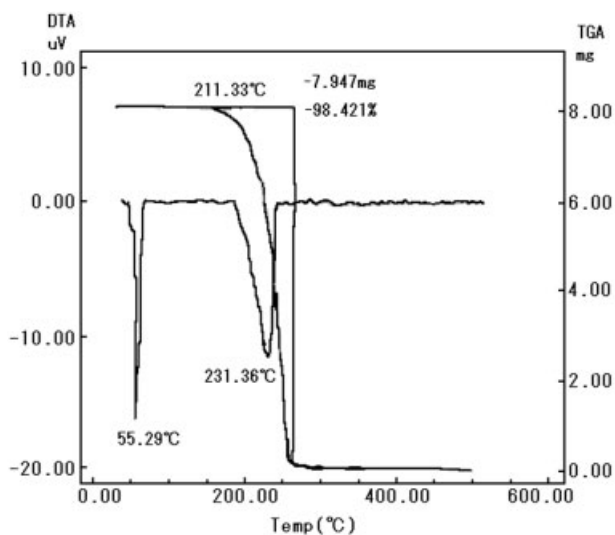


Figure 1 TGA and DTA curves for 11-bromoundecanoic acid.

The amount of carboxylate at the end of the polymer chains was measured by back-titration of hydrochloric acid. That is, excess amount of a 0.100M hydrochloric acid was added to carboxylate to convert it to carboxylic acid. Hydrochloric acid remaining was titrated with a 0.01M sodium carbonate standard solution. Prior to the experiment, we could confirm that the presence of carboxylic acid slightly interferes with the measurement of hydrochloric acid.

Thermal characteristics and the decomposition temperature were measured by a Shimadzu DTA-50 thermal analysis apparatus. The presence of an ester group was ascertained from the infrared spectrum.

RESULTS AND DISCUSSION

The effect of various solvents on condensation polymerization for 11-bromoundecanoate was investigated using DMF, DMSO, DMAC, water, and ethylene glycol. In such a reaction, cyclization, the formation of lactone, and release of hydrogen bromide may occur alongside the intended reaction, polycondensation. Polycondensation using DMF, DMSO, DMAC, ethylene glycol, and water as solvents was carried out. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves for the products and raw materials were prepared as shown in Figures 1–3. The products prepared in DMAC and water are selected as control samples. Figure 1 shows that 11-bromoundecanoic acid has a sharp exothermic peak at 55.29°C, which seems to be the melting point. As shown in Figure 2, the peak is also found in the curves for the product synthesized in DMAC. The formation of 11-bromoundecanoic acid by eliminating hydrogen bromide, followed by neutralizing 11-bromoundecanoate, might cause the appearance of the peak. Further,

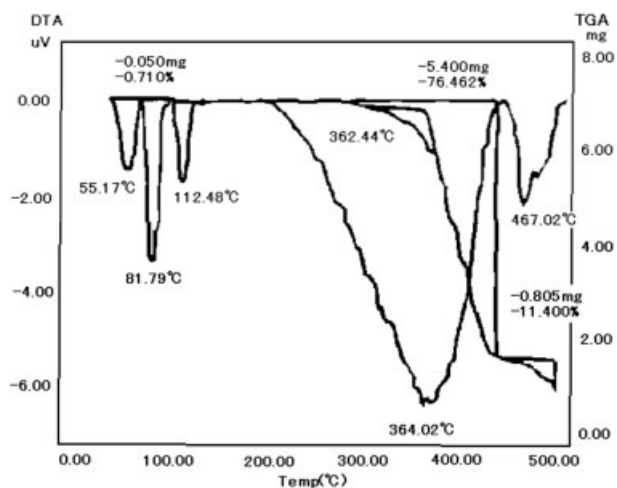


Figure 2 TGA and DTA curves for the product at 90°C for 72 h in DMAC.

there are two peaks at 81.79 and 112.48°C in the curve. They appear to be other substances of low melting point, produced in side reactions. These products, possibly acids, can also be similarly formed by the neutralization of products of low molecular weight. It is very difficult to extend their chain lengths. It was found that products made in DMF and DMSO showed peaks at similar positions, though there were differences in strength. The product made in aqueous media results in a monotonic curve. It seems that only polycondensation proceeds as the main reaction. That is, only a polymer is formed.

Another experiment on determining the degree of polymerization was carried out for products made by using DMAC, DMF, DMSO, ethylene glycol, and water at various temperatures. Degrees of polymerization were calculated from both the amount of bromide ion formed in media and from the back-titration value of the end group assay of carboxylate. Discernible

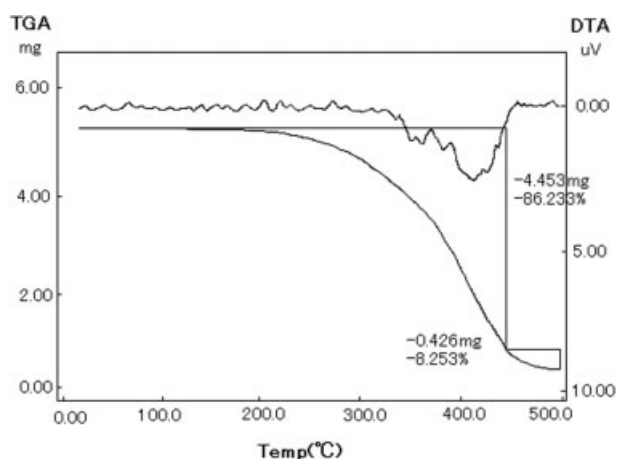


Figure 3 TGA and DTA curves for the product at 70°C for 240 h in aqueous media.

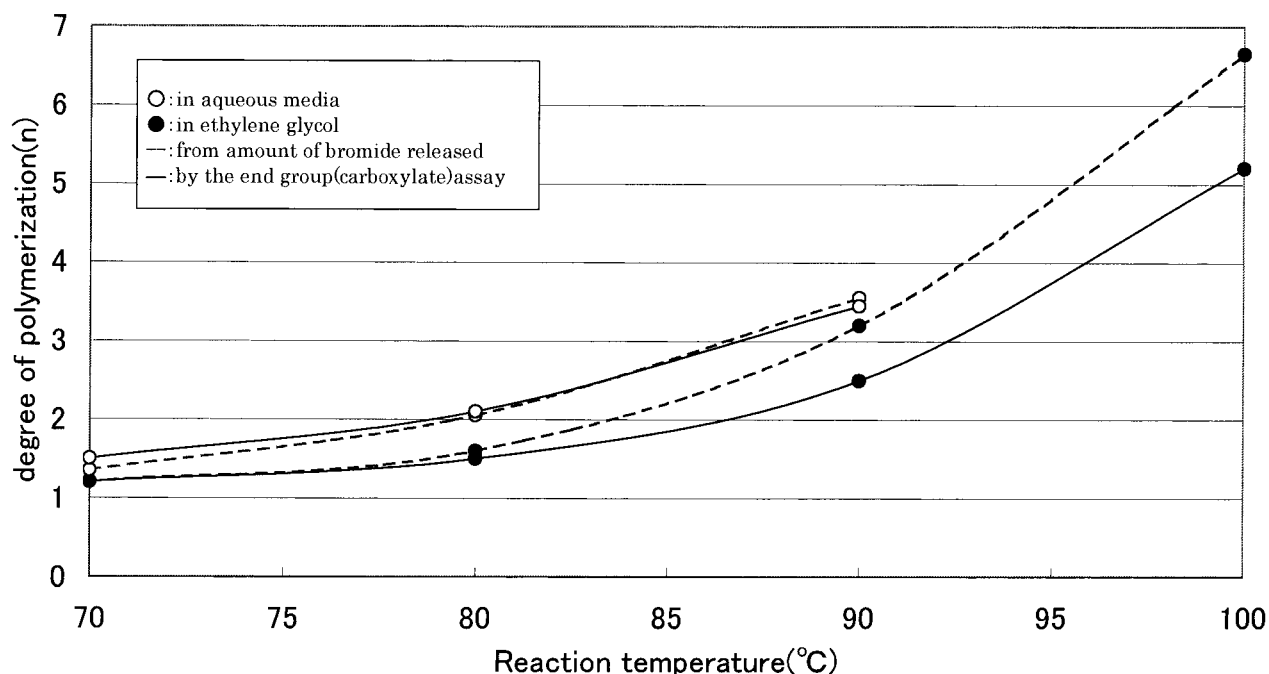


Figure 4 Relation between reaction temperature and degree of polymerization.

differences were observed, however, between the values for the degree of polymerization calculated for the sample in DMAC, DMF, and DMSO. That means the degree of polymerization calculated from the amount of bromide ion was appreciably greater than that calculated from the back-titration value of the carboxylate end group. The difference is distinctly noticeable in reactions at temperatures above 80°C in aprotic solvents, and at 100°C in ethylene glycol. If hydronium ions existing as hydrogen bromide decompose solvents without being consumed to neutralize carboxylate, confusion will result in the stoichiometric relationship between the remaining amounts of bromide ions and carboxylate, affecting accurate measurement of polymerization. The solvents used are decomposed by acids. So hydronium ions are consumed without completely neutralizing the carboxylate. In the case of ethylene glycol at temperatures higher than 90°C, a relatively large difference was observed between both values, as shown in Figure 4. Perhaps the hydrogen bromide generated reacts with ethylene glycol to form dibromoethane. At any rate, the cause of inconsistencies can be attributed to the formation and release of hydrogen bromide. As a result, we judged that solvents such as DMSO, DMF, and DMAC are unsuitable for polymerizing bromoundecanoate. Consequently, we abandoned the experiment in aprotic solvents. In aqueous solutions of bromoundecanoate, the degree of polymerization for polymers calculated by the amount of bromide ion formed is far closer to the value for the end group assay of carboxylate.

At lower temperatures than 90°C in aqueous media or ethylene glycol, the possibility of side reactions, cyclization, or releasing is never denied, since there is a similar relationship between the end group carboxylate and bromine assays for polycondensation, the cyclization, and release. However, it is estimated that the reaction mechanism is different for each case. Cyclization, the formation of lactone, and the release of hydrogen bromide should proceed as a first-order reaction, while polycondensation should occur as a second-order reaction. Next, the order of the reactions was investigated by using the ethylene glycol solution containing 0.025–0.045M of 11-bromoundecanoate at 70°C. The results are shown in Figure 5 and Figure 6. We experimentally determined this to be a second-order reaction. Therefore, the reaction must proceed according to the S_N2 mechanism, making it a bimolecular reaction and thus a condensation reaction. It seems that this bimolecular reaction proceeds similarly in aqueous media. Water is well suited to polycondensation. Although the temperature of the aqueous media cannot rise above the boiling point, side reactions are not considered a problem.

Next, we investigated how the concentration of bromoundecanoate affected polycondensation, using water as a solvent. Exactly 250 mg (0.922 mmol) of undecanoate was added to 1, 2, 5, and 10 mL of water, each in a 50 mL sample bottle, and each sample bottle was kept in the water baths maintained at 70, 80, and 90°C for 6 h. When a small amount of the solvent, such as 1 mL was used, high degrees of polymerization may be achieved because of the higher probability of

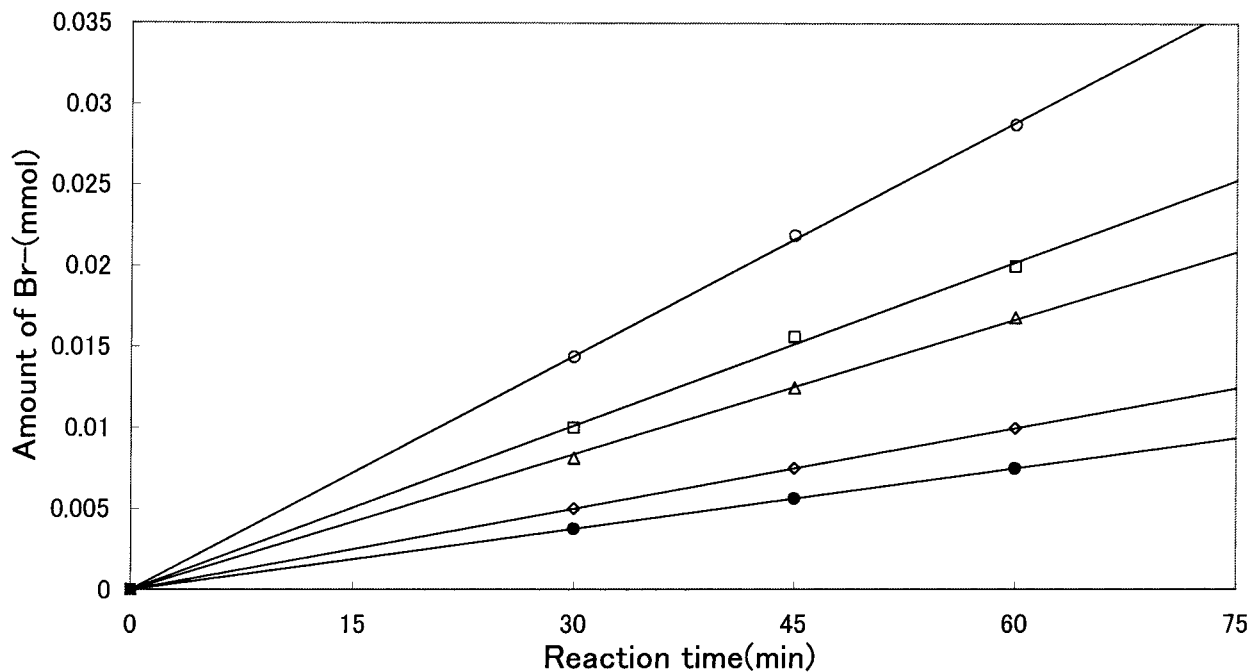


Figure 5 Relation between amount of bromide ion released and reaction time.

mutual collisions for the monomers. Using 10 mL of water, desirable long-chain polymers were obtained because monomers and polymers had more space to move.

Next, we investigated the thermodynamics. Several thermodynamic parameters were calculated by the Eyring plots from the relationship between the bromide ions, formed by the condensation, and the reac-

tion temperature. The measurement was carried out at six points between 60 and 75°C, using the 0.025M lithium bromoundecanoate aqueous solution and the ethylene glycol solution. The results are shown in Table I. The condensation in ethylene glycol takes place with a higher value of ΔH than that in the aqueous media. The enhancement of dissociation ac-

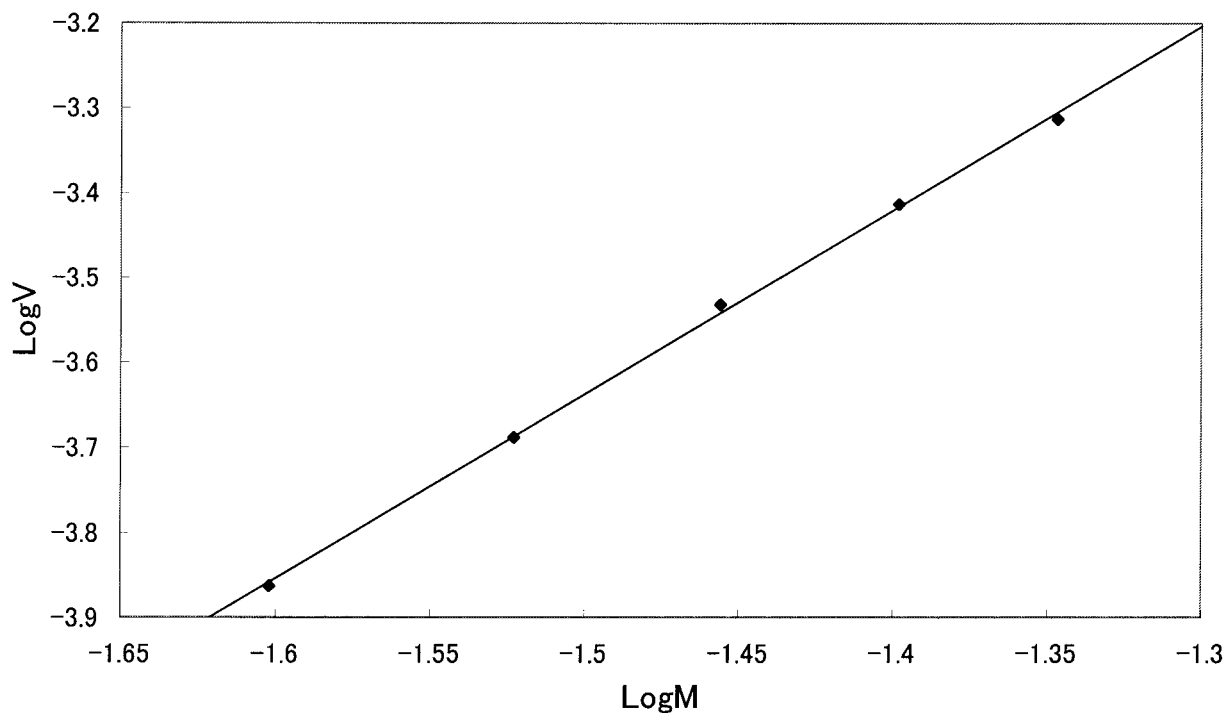


Figure 6 Determination of reaction order.

TABLE I
Thermodynamic Parameters for Condensation

Solvent	ΔH (kcal mol ⁻¹)	ΔS (cal K ⁻¹ mol ⁻¹)	ΔG (kcal mol ⁻¹)	k ₃₄₃ s ⁻¹
EG	21.0	-4.57	22.6	0.030
H ₂ O	20.6	-2.00	21.6	0.211

counts for the easiness of the condensation in aqueous media. The difference between the rate of condensation in aqueous media and that in ethylene glycol media is clearly discerned: that is, the rate in aqueous media is 7 times greater than that in the ethylene glycol media. Using of aqueous media is far more advantageous. The difference in ΔS allows the condensation to take place more easily and faster in aqueous media than in ethylene glycol. Table I shows ΔS to be negative and ΔG to be positive, meaning that the condensation reaction proceeds exothermically and not spontaneously.

Finally, polycondensation to obtain a favorable polymer was carried out for 10 days in a water bath, kept at 70°C, using 25 mL of 0.05M 11-bromoundecanoate. The degree of polymerization for the product was measured by three means: the determination of carboxylate and bromine end groups and determination of bromide ions formed in aqueous media. Every calculation shows the degree of polymerization to be 23.

The product is soluble in THF, degrades at about 300°C and simultaneously disperses. The film of the product is transparent but brittle.

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