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Thermal reactions of alkali 4-(bromomethyl)benzoate–bromoacetate binary systems in the bulk

Mari Inoki, Fumihiko Akutsu,* Fang Fang, Emi Mitsui, Yoshio Kasashima and Kiyoshi Naruchi

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho 1–33, Inage-ku, Chiba-shi, 263, Japan

Thermal reactions of alkali 4-(bromomethyl)benzoate–bromoacetate (4-BMBA–BA) binary systems in the bulk have been investigated. Those of equimolar sodium and potassium 4-BMBA–BA result in copolycondensation in the solid state to give a copolyester. However, reaction of the equimolar lithium salts at 210 °C for 1 h, followed by esterification, afford methyl 4-(bromomethyl)benzoyloxyacetate as a cross-condensed dimer in 30% yield. The yield increases in the initial hour, but then gradually decreases due to the formation of oligomers. The X-ray diffraction pattern of the Li salts (powder method) indicates a new crystal phase, which is different from the individual patterns of lithium bromoacetate and lithium 4-(bromomethyl)benzoate. The formation of the new crystal phase contributes to a reduced melting point, and the Li salts react in the liquid phase without pyrolysis, causing cross-condensed dimerization.

Introduction

We previously reported that the solid-state thermal reactions of alkali salts of binary unsaturated carboxylic acids systems, such as acrylic acid (AA)–methacrylic acid (MA),[1,2] crotonic acid–MA,[3,4] but-3-enoic acid–MA[5] and 3-methylbut-3-enoic acid–MA,[6] caused selective cross-coupled dimerization. This was attributed to the formation of a new crystal phase for the equimolar binary salts which differs from that of the individual salts, and to retention of the crystallinity of the reaction system owing to the formation of solid solution crystals during dimerization. On the other hand, it was found that the thermal reactions of sodium or potassium salts of brominated carboxylic acids, such as 2-bromobutanoic acid,[7] 2-bromopropanoic acid[8] and 3- and 4-(bromomethyl)benzoic acid[9] in the solid state caused the polycondensations to produce polyesters, whereas these lithium salts either did not react or possessed much lower reactivity.

In this study, the thermal reactions of binary alkali 4-(bromomethyl)benzoate–bromoacetate (4-BMBA–BA), as examples of binary systems of alkali brominated carboxylates, were investigated in the bulk. The thermal reactions of the binary salts of halogenated carboxylic acids have not yet been reported.

Results and discussion

Thermal reactions of alkali bromoacetates

We previously reported that the thermal reactions of sodium and potassium 4-BMBAs in the solid state gave a polyester of inherent viscosity *ca.* 0.020 $dm^3\ g^{-1}$, and that reaction of the lithium salt did not proceed.[9] On the contrary, it was reported that pyrolysis of sodium chloroacetate under reduced pressure gave glycolide,[10,11] and that sodium bromoacetate reacted in *N*,*N*-dimethylformamide to afford oligo(glycolic acid).[12] Other attempts at thermal reactions of alkali halogenoacetates have been reported,[13–15] but an identification of the products was not followed up. Thus, thermal reactions of alkali bromoacetates in the bulk or in the solid state have not yet been studied in detail.

Thermal analysis by means of thermogravimetry–differential thermal analysis (TG–DTA) of alkali BAs was performed. DTA curves of Na– and K–BA showed exothermic peaks at 205 and 189 °C, respectively. However, the curve for Li–BA exhibited an endothermic peak at 217 °C and showed no exothermic peak. This suggests that Na– and K–BAs may react in the solid state, but that Li–BA does not react in the solid state and melts instead. The results are summarized in Table 1.

Table 1 Thermal analysis of the salts by TG–DTA

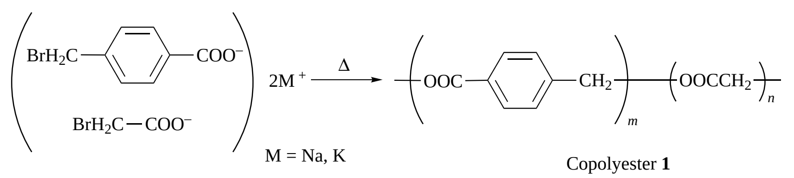
Salts	Exothermic temperature[a]/°C	Endothermic temperature[a]/°C	Thermal decomposition temperature[b]/°C
Li–BA	—	217	255
Na–BA	205	—	263
K–BA	189	—	252
Li–4-BMBA[c]	—	305	304
Na–4-BMBA[c]	294	—	388
K–4-BMBA[c]	264	—	390
Li–(BA–4-BMBA)	—	208,242	265
Na–(BA–4-BMBA)	191	—	211
K–(BA–4-BMBA)	162	—	317

[a] Measured by DTA. Heating rate, 10 K min^{-1}. [b] Measured by TG. Heating rate, 10 K min^{-1}. [c] Data of alkali 4-BMBAs were quoted from ref. 9.

Thermal reactions of alkali bromoacetates in the bulk were carried out. Li–BA did not react below 190 °C, and carbonized at 200 °C. The product from Na–BA was dissolved in hexafluoroisopropyl alcohol (HFIP) and the solution was poured into hexane. The residue was purified and identified by spectroscopic data and elemental analysis and shown to be poly(glycolic acid). The product from K–BA was also poly(glycolic acid). The inherent viscosities were found to be in the range 0.035–0.064 $dm^3\ g^{-1}$. K–BA was more unstable, and carbonized at 150 °C. The results are indicated in Table 2. Thus, the thermal reactions of Na– and K–BAs caused polycondensation but Li–BA did not react.

Preparation of the binary monomeric salts

The equimolar binary salts, such as Li–(4-BMBA–BA), Na–(4-BMBA–BA) and K–(4-BMBA–BA), were prepared not by mixing the individual salts, but by neutralizing a binary acid solution with a methanolic solution of the corresponding metal



4-BMBA–BA

M = Na, K

Copolyester **1**

Scheme 1

Table 2 Thermal reactions of alkali bromoacetates

		Poly(glycolic acid)	
Salts	T/°C	Yield (%)	η_{inh}/dm^3 g^{-1} [a]
Li	190	n.r.[b]	
Li	200	Car[c]	
Na	170	82	0.059
Na	180	89	0.064
Na	190	Car[c]	
K	130	85	0.035
K	140	95	0.040
K	150	Car[c]	

[a] Inherent viscosity, measured in HFIP at a concentration of 5.0 g dm^{-3} at 30 °C. [b] No reaction. [c] Carbonization.

Table 3 Thermal reactions of Na– and K–(4-BMBA–BA)

		Copolyester **1**	
Salts	T/°C	Yield (%)	η_{inh}/dm^3 g^{-1} [a]
Na	150	45	0.012[b]
Na	160	65	0.019[b]
Na	180	97	0.016[b]
Na	190	100	0.016[b]
Na	200	Car[d]	
K	150	80	0.019[c]
K	160	78	0.019[c]
K	170	Car[d]	

[a] Inherent viscosity, measured at a concentration of 5.0 g dm^{-3} at 30 °C. [b] Measured in dimethyl sulfoxide. [c] Measured in 1,1,2,2-tetrachloroethane–phenol (40/60 by weight). [d] Carbonization.

hydroxide. The salts obtained were dried under reduced pressure and the products were identified by elemental analysis.

DTA curves of the binary Na and K salts indicated exothermic peaks at 191 and 162 °C, respectively. Endothermic peaks were not found below those exothermic peak temperatures. The thermal decomposition temperatures, determined by TG, were found to be 211 and 317 °C, respectively. However, a DTA curve of the binary Li salts showed no clear exothermic peak, but indicated instead two endothermic peaks at 208 and 242 °C. These endothermic peaks may be due to the existence of two crystal systems, which melted independently. The results are tabulated in Table 1. Thus, the thermal behaviour of the equimolar binary salts was different from that of the individual salts. The thermal behaviour was further investigated by means of differential scanning calorimetry (DSC) in order to confirm the melting behaviour of Na– and K–(4-BMBA–BA)s. DSC curves of the Na and K salts showed no endothermic peak for melting. These facts suggest that Na– and K–(4-BMBA–BA)s react in the solid state without melting and decomposition.

Thermal reactions of equimolar Na– and K–(4-BMBA–BA)s

The thermal reactions of equimolar Na–(4-BMBA–BA) were carried out at 150–200 °C for 2 h under reduced pressure. The product at 200 °C was carbonized. The other products were dissolved in dimethyl sulfoxide (DMSO) or a mixed solvent of 1,1,2,2-tetrachloroethane–phenol (40/60 by weight) because they were insoluble in other solvents, and the solution was poured into methanol to initiate precipitation. After being reprecipitated, the products were identified by spectroscopic data as copolyester **1**, of which the molar ratio of 4-BMBA unit/BA unit was *ca.* 1/1. Similar to the reaction of the Na salts, that of equimolar K–(4-BMBA–BA) also afforded copolyester **1**. The product of the reaction at 170 °C was carbonized. The inherent viscosities of the copolyesters obtained lay in the range 0.012–0.019 dm^3 g^{-1}, and the yields were *ca.* 80%. The results are summarized in Table 3. Thus, the thermal reactions of Na– and K–(4-BMBA–BA) caused copolycondensation, as shown in Scheme 1.

Thermal reactions of Li–(4-BMBA–BA)s

The thermal reaction of equimolar Li–(4-BMBA–BA) was conducted at 210 °C for 2 h under reduced pressure. Unlike the product of Na– or K–(4-BMBA–BA), the reaction mixture was completely soluble in water. This solution was acidified with hydrochloric acid and extracted with diethyl ether. After being esterified with diazomethane, the product was subjected to analysis by gas chromatography (GC). The gas chromatogram of the esterified product indicated a new single peak and the peak of methyl 4-BMBA, but any peak due to methyl BA disappeared. The product corresponding to the new peak was isolated by silica gel column chromatography and identified by spectroscopic data as methyl 4-(bromomethyl)benzoyloxyacetate (the methyl ester of cross-condensed dimer **2**). The yield of cross-condensed dimer **2**, determined by GC using an internal standard, was 22%. The number-average molecular weight of the esterified product (except for the monomeric ester), measured by gel-permeation chromatography, was 600. The yield of the co-oligoester was 73%.

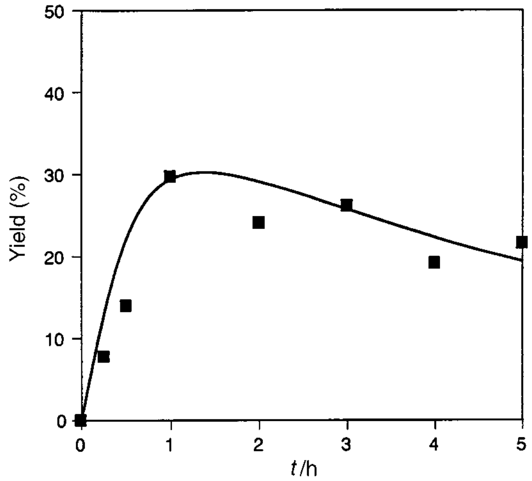
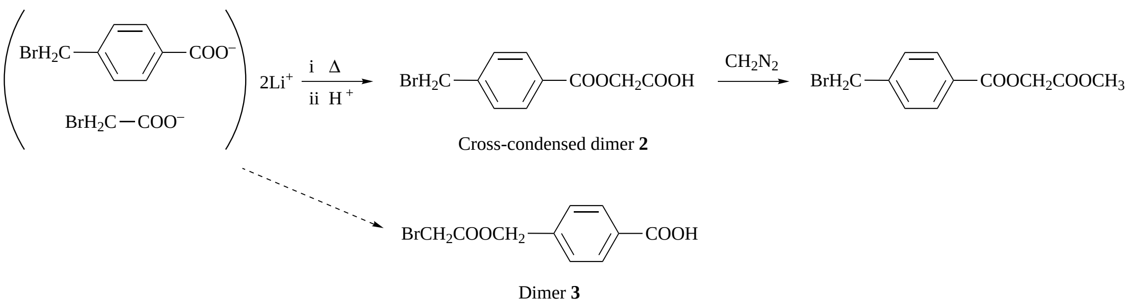


Fig. 1 Thermal reaction of Li–(4-BMBA–BA) at 210 °C

The thermal reactions of Li–(4-BMBA–BA) were conducted at 180–230 °C for 2 h. The product of the reaction at 230 °C was carbonized. The yield of dimer **2** was greatest in the reaction at 210 °C (22%), but in the reaction temperature range between 190 and 220 °C the yield decreased slightly. However, in the reaction at 180 °C, the yield was significantly reduced (8%). The results are tabulated in Table 4.

The yield of dimer **2** in the reaction at 210 °C is shown as a function of reaction time in Fig. 1. The highest yield was 30% after reaction for 1 h, and then the yield lowered gradually.



Scheme 2

Table 4 Thermal reactions of Li–(4-BMBA–BA)

T/°C	Yield of **2** (%)[a]	Yield of co-oligoester (%)[b]	M_n[c]
180	8	—	
190	17	—	
200	20	—	
210	22	74	600
220	18	73	640
230	Car[d]		

[a] Determined by gas chromatography using an internal standard. [b] Containing **2**. [c] Number-average molecular weight of an co-oligoester containing **2**, determined by gel-permeation chromatography. [d] Carbonization.

Whereas the peak corresponding to BA in the gas chromatogram disappeared after reaction for an initial hour, 30% of 4-BMBA remained after reaction for 5 h. The low yield of dimer **2** was attributed to conversion to oligomers and the low reactivity of Li–4-BMBA.

We have reported that the solid-state thermal polycondensations of alkali 2-bromopropanoates and alkali 4-BMBAs proceed mainly according to an S_N1 reaction mechanism, refs. 8 and 9, respectively. Therefore, it was expected that if cross-condensed dimerization occurs in this reaction, dimer **3** in Scheme 2 would be formed because of the higher reactivity of the bromo group at the benzyl position in 4-BMBA. However, only the cross-condensed dimer **2** was obtained, as shown in Scheme 2. It was considered that the reaction of Li–(4-BMBA–BA) proceeded *via* a mechanism different from that of the solid-state thermal polycondensation, because Li–(4-BMBA–BA) reacted mainly in the liquid phase. In the initial stage, Li–(4-BMBA–BA) may partially react in the solid state to give dimer **3** which immediately converts to oligomers. In the reaction of the Li salts at 210 °C for 15 min, the recovered ‘yield’ of 4-BMBA was 46% although the yield of dimer **2** was 7%. It was considered that the oligomers formed in the initial stage acted as impurities, lowering the melting point of the reaction system and allowing dimer **2** to be obtained in small quantities at a reaction temperature below 200 °C.

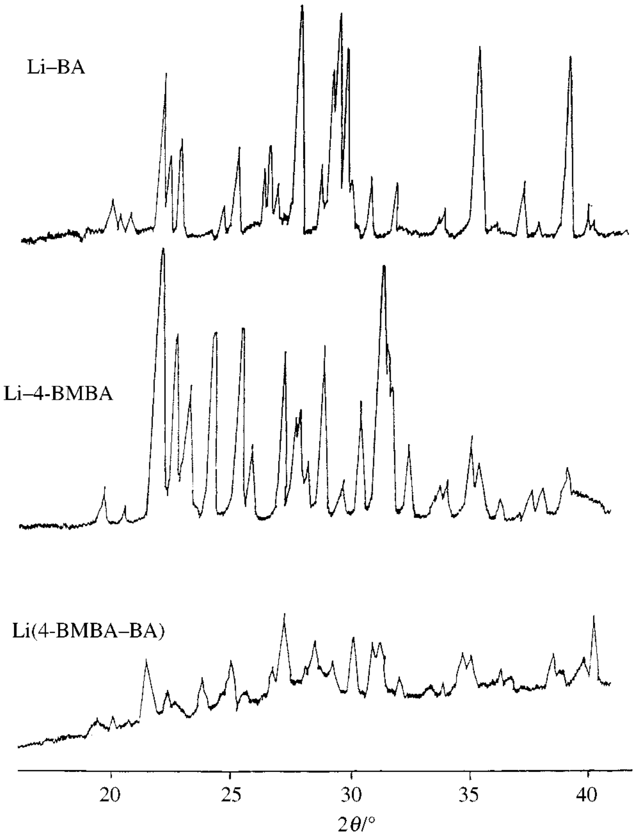


Fig. 2 X-ray diffraction patterns of Li–BA, Li–4-BMBA and Li–(4-BMBA–BA)

The X-ray diffraction pattern of Li–(4-BMBA–BA) by the powder method indicated a crystalline salt, which was different from the individual patterns of Li–BA and Li–4-BMBA, as illustrated in Fig. 2. This suggested the formation of a new crystal phase different from that of the individual salts. However, as mentioned above, the DTA curve of Li–(4-BMBA–BA) showed two endothermic peaks. For Li–(4-BMBA–BA) in the solid state there may exist mixed crystals of Li–4-BMBA with Li–BA and amorphous Li–4-BMBA. Most likely, formation of the mixed crystals would then make the remaining Li–4-BMBA amorphous, and the thermal reaction would occur mainly as the mixed crystals melted, amorphous Li–4-BMBA either partially reacting or not at all. In addition, the fact that the dimer obtained was not **3** but **2** indicated that Li–4-BMBA possessed lower reactivity. Therefore, after reaction at 210 °C for 5 h, 30% of Li–4-BMBA remained. It was found that Li–4-BMBA melted at 305 °C with decomposition and that Li–BA melted at 215 °C with decomposition. Since the mixed crystals—indicating the new crystal phase—showed a lower melting point, Li–BA and Li–4-BMBA could react in the liquid phase at the lower temperature.

The conversions into dimer **2** at 210 °C for 2 h are shown as functions of the composition of Li–(4-BMBA–BA) in Fig. 3. When the molar ratios of 4-BMBA/BA were 3/7, 2/8 and 1/9, the products were carbonized and the X-ray diffraction patterns indicated the presence of Li–BA. The carbonization of the products was attributed to reaction in the crystals of Li–BA. When the molar ratios were 5/5 and 4/6, X-ray diffraction patterns showed the new crystal phase to be different from that of the individual salts, and the conversions into dimer **2** were much higher. On the contrary, when the molar ratios were 9/1, 8/2, 7/3 and 6/4, X-ray diffraction patterns indicated the presence of Li–4-BMBA, and the conversions into the dimer were low. It seems that these low conversions may be due to more stable crystals of Li–4-BMBA.

Conclusions

The thermal reaction of equimolar K– and Na–(4-BMBA–BA)s led to copolycondensation in the solid state, producing a copolyester. However, reaction of equimolar Li–(4-BMBA–BA)

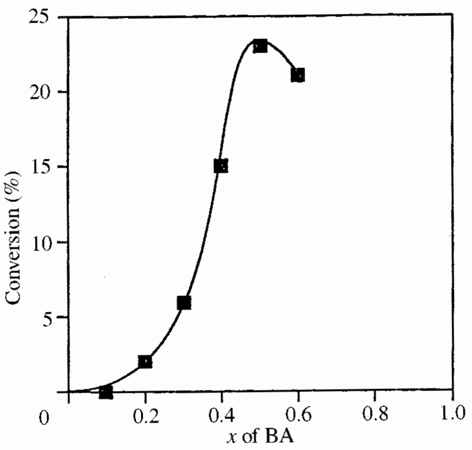


Fig. 3 Conversion of Li–(4-BMBA–BA) into dimer **2** at 210 °C for 2 h

proceeded in the liquid phase, and caused cross-condensed dimerization giving **2** with oligocondensation, without the production of dimer **3** or the homo-dimers. The formation of a new crystal phase for the binary Li salts lowered the melting point. The characteristic cross-condensed dimerization was attributed to the lower reactivity of Li–4-BMBA than that of Na– or K–4-BMBA, and to the melting behaviour of the binary Li salts. The mechanism of the dimerization is different from that of the cross-coupled dimerization of binary unsaturated carboxylates in the solid state.

Experimental

Measurements

IR spectra were recorded on a Hitachi 270–30 spectrophotometer. ^{1}H NMR spectra were recorded on a 500 MHz FT-NMR spectrometer (JEOL JNM-GSX500 or JNM-LA500). J values are given in Hz. ^{13}C NMR spectra were recorded on a 125 MHz FT-NMR spectrometer (JEOL JNM-GSX500 or LA500). Wide angle X-ray diffraction patterns were obtained for specimens on Rigaku XG X-ray diffraction apparatus with Cu-K$_\alpha$ radiation (35 kV, 20 mA) by the powder method. For GC measurements, a Hitachi 263-50 instrument was used under the following conditions: column packing, silicone SE-30 (3 mm × 2 m); column temperature, 50–250 °C; heating rate, 10 K min^{-1}, carrier gas, nitrogen; gas flow, 30 cm^3 min^{-1}. Mass spectra were recorded on a JEOL JMS-HX110 mass spectrometer. Thermoanalytical measurements by means of DSC (MAC Science DSC 3100) and TG–DTA (MAC Science TG–DTA 2000) were carried out under the following conditions: heating rate, 10 K min^{-1} in a nitrogen atmosphere. GPC measurements were performed on a TOSOH HLC-802UR high-speed liquid chromatograph equipped with a polystyrene gel column and refractive index (RI) detector (solvent: THF; concentration: 2.0 g dm^{-3}; calibration: polystyrene standards with narrow molecular weight distribution).

Preparations and thermal reactions of alkali bromoacetates

Li–, Na– and K–BAs were prepared by neutralizing bromoacetic acid with the corresponding metal hydroxide in methanol. Methanol was removed and the product was washed with diethyl ether and dried under reduced pressure in the presence of phosphorus pentaoxide. The salts obtained were identified by elemental analysis. Li–BA: Found: C, 16.5; H, 1.6. Calc. for $C_2H_2O_2BrLi$: C, 16.58; H, 1.39%. Na–BA: Found: C, 14.6; H, 1.3. Calc. for $C_2H_2O_2BrNa$: C, 14.93; H, 1.25%. K–BA: Found: C, 13.5; H, 1.2. Calc. for $C_2H_2O_2BrK$: C, 13.57; H, 1.14%.

1.0 g of the monomeric salt was placed in a Pyrex tube, dried under reduced pressure for 1 h prior to reaction and heated in an oil bath under reduced pressure for 2 h. The products from Na– and K–BAs were dissolved in HFIP (Central Glass Co., Ltd.), filtered through a glass filter to remove sodium bromide and the solution was poured into methanol to initiate precipitation. The resulting precipitate was washed with water and dried under reduced pressure. The product was purified by reprecipitation; η_{inh} = 0.64 dm^3 g^{-1} (measured in HFIP at a concentration of 0.5 g dm^{-3} at 30 °C). ν_{max}(KBr)/cm^{-1} 1744 (C=O) and 1156 (C–O). δ_H(500 MHz; [$^2H_2$]HFIP; 40 °C) 5.19 (s). δ_C(125 MHz; [$^2H_2$]HFIP) 61.96 (–CH$_2$–), 169.62 (C=O). Poly(glycolic acid): Found: C, 41.6; H, 3.3. Calc. for $(C_2H_2O_2)_n$: C, 41.39; H, 3.47%.

Preparation of the binary monomeric salts

4-BMBA was prepared by bromination of 4-methylbenzoic acid using *N*-bromosuccinimide.[9,16–18] Equimolar binary Li, Na and K salts were used as monomers. The monomeric salts were prepared by neutralizing an equimolar binary acid solution with a methanol solution of the corresponding metal hydroxide using Phenolphthalein as indicator. Methanol was removed and the product was washed with diethyl ether and dried under reduced pressure in the presence of phosphorus pentaoxide. The salts obtained were identified by elemental analysis. Li–(4-BMBA–BA): Found: C, 33.2; H, 2.2. Calc. for $C_{10}H_8O_4Br_2Li_2$: C, 32.83; H, 2.20%. Na–(4-BMBA–BA): Found: C, 30.0; H, 2.0. Calc. for $C_{10}H_8O_4Br_2Na_2$: C, 30.18; H, 2.02%. K–(4-BMBA–BA): Found: C, 27.7; H, 1.8. Calc. for $C_{10}H_8O_4Br_2K_2$: C, 27.92; H, 1.87%.

Thermal reactions of Na–(4-BMBA–BA) and K–(4-BMBA–BA)

The appropriate monomeric binary salt (1.0 g) was placed in a Pyrex tube, dried under reduced pressure for 1 h prior to reaction and heated in an oil bath under reduced pressure at 150–200 °C for 2 h. The product was dissolved in a mixed solvent of 1,1,2,2-tetrachloroethane–phenol (40/60 by weight) or in DMSO, filtered through a glass filter to remove alkali bromides and poured into methanol to initiate precipitation. The resulting precipitate was washed with methanol and dried under reduced pressure. The product was purified by reprecipitation. ν_{max}(KBr)/cm^{-1} 1762 (C=O), 1720 (C=O), 1274 (C–O), 1174 (C–O) and 1100 (C–O). δ_H(500 MHz; [$^2H_6$]DMSO, 100 °C) 4.84 (2H, s), 4.95 (2H, s), 5.29 (2H, s), 5.43 (2H, s), 7.50–7.59 (8H, m). δ_C(125 MHz; [$^2H_6$]DMSO, 80 °C) 60.46 (–COO*C*H$_2$COO–), 60.83 (–COO*C*H$_2$COO–), 65.11 (–Ar*C*H$_2$COO–), 66.42 (–Ar*C*H$_2$COO–), 127.11 (Ar), 127.36 (Ar), 128.83 (Ar), 129.01 (Ar), 129.10 (Ar), 129.18 (Ar), 140.19 (Ar), 140.78 (Ar), 166.11 (C=O), 171.88 (C=O).

Thermal reactions of Li–(4-BMBA–BA)

The appropriate monomeric binary lithium salt was placed in a Pyrex tube, dried under reduced pressure for 1 h prior to reaction and heated at 180–230 °C for 2 h under reduced pressure. The reaction mixture was dissolved in water, acidified with hydrochloric acid and extracted with diethyl ether. The ether layer was dried with anhydrous sodium sulfate overnight. After esterification with diazomethane the product was subjected to analysis by GC. Isolation of the dimer was carried out by silica gel column chromatography (ethyl acetate–hexane, 1:4) of the esterified product yielding methyl 4-(bromomethyl)benzoyloxyacetate (methyl ester of cross-condensed dimeric acid **2**); *m/z* 289 (MH$^+$+2), 287 (MH$^+$); δ_H(500 MHz; CDCl$_3$) 3.79 (3H, s), 4.50 (2H, s), 4.86 (2H, s), 7.48 (2H, d, J 8.5), 8.08 (2H, d, J 8.5); δ_C(125 MHz; CDCl$_3$) 32.09 (Br*C*H$_2$–), 52.34 (–COO*C*H$_3$), 61.14 (–COO*C*H$_2$COO–), 120.09 (Ar), 130.42 (Ar), 130.45 (Ar), 143.25 (Ar), 165.36 (Ar*C*OO–), 168.18 (–*C*OOCH$_3$).

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