Thermal dimerization of alkali and alkaline earth acrylate–but-3-enoate and methacrylate–but-3-enoate binary systems in the solid state

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The solid state thermal reaction of binary salts obtained from a solution of an equimolar mixture of alkali or alkaline earth salts of but-3-enoic acid and methacrylic acid (3-BA–MA), after conversion to the methyl ester, gave mainly dimethyl (*E*)-hex-1-ene-1,5-dicarboxylate as a novel cross-coupled dimer. The highest conversion (62.2%) to the cross-coupled dimer was obtained using the potassium salts on heating at 230 °C for 2 h. Similarly, the methyl ester of the cross-coupled dimer, dimethyl (*E*)-pent-1-ene-1,5-dicarboxylate, was obtained from the salts of 3-BA and acrylic acid (AA), however a small amount on an isomeric ester dimethyl (*E*)-pent-2-ene-1,5-dicarboxylate was also obtained. The X-ray diffraction patterns of potassium 3-BA–MA and potassium 3-BA–AA indicate the presence of a new phase, different from that of the individual salts. The selective cross-coupled dimerization, without rearrangement of 3-BA to crotonic acid, polymerization and crosslinking, was due to the new crystal phase of the binary salts as well as to the formation of solid solution crystals between the monomeric salts and the dimeric salt.

Introduction

We have previously studied the solid state thermal reaction of alkali and alkaline earth salts of methacrylic acid (MA), and reported that the reaction produces several oligomers, such as dimers, trimers and tetramers, or a polymer, and that the formation of the oligomers depends upon the crystallinity of the salts and the stability of the crystal.[1–6] The solid state thermal reaction of alkali salts of crotonic (*trans*-but-2-enoic) acid (CA) has also been investigated.[7,8] From the sodium salt of CA, the dimer hex-1-ene-3,4-dicarboxylic acid was obtained quantitatively. The selective production of the dimer was induced by the formation of solid solution crystals during dimerization.[7] However, three isomers of the dimer were obtained from the potassium salt because the crystal structure of the monomeric salts was destroyed as the dimerization proceeded.[8]

In addition, we have investigated the solid state thermal reaction of salts of binary acid systems.[9,10] From equimolar solutions of the sodium salts of acrylic acid and crotonic acid (AA–CA) or from those of methacrylic acid and crotonic acid (MA–CA), cross-coupled dimers were obtained. These were due to the formation of a new crystal phase for the equimolar binary salts which differs from that of individual salts in that the crystallinity of the reaction system is kept by the formation of solid solution crystals during dimerization.[10]

In this study, the thermal reactions of the binary salts of but-3-enoic acid and methacrylic acid (3-BA–MA) and of 3-butenoic acid and acrylic acid (3-BA–AA) were investigated. It is known that salts of but-3-enoic acid can rearrange into crotonic acid in solution. We found that in the solid state, the thermal reaction of sodium but-3-enoate produced mainly dimers of but-3-enoic acid without any rearrangement to crotonic acid, while that of the alkaline earth salts or the potassium salts proceeded with rearrangement to produce several dimers, such as dimers of crotonic acid and a cross-coupled dimer of crotonic acid–but-3-enoic acid.[11,12] The crystal state of the reaction system was found to contribute to the rearrangement in the solid state.

Experimental

Measurements

IR spectra were recorded on a Hitachi 270–30 spectrophotometer. ^1H NMR spectra were obtained with a 400 MHz FT-NMR spectrometer (JEOL JNM-GSX400); *J* values are given in Hz. ^{13}C NMR spectra were obtained with a 125 MHz FT-NMR spectrometer (JEOL JNM-GSX500). Wide angle X-ray diffraction patterns were obtained for specimens on a Rigaku Denki XG X-ray diffraction apparatus with Cu-Kα radiation (35 kV, 20 mA). For gas chromatography (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}. The mass spectra were recorded on a JEOL JMS-HX110 mass spectrometer. Thermoanalytical measurement by means of differential scanning calorimetry (DSC; Rigaku DSC8230D) was carried out under the following conditions: heating rate, 10 K min^{-1}; in a nitrogen atmosphere.

Materials

Lithium (Li), sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), barium (Ba) and strontium (Sr) salts of binary acids were used as monomers. The monomeric salts were prepared by neutralizing a binary acid solution of a prescribed molar ratio with aqueous metal hydroxide using phenolphthalein as an indicator. After the complete removal of water by distillation, the obtained salt was dried under reduced pressure at 60 °C in the presence of phosphorus pentoxide.

Elemental analyses. Li(3-BA–MA) Found: C, 52.2; H, 5.5. Calc. for $C_8H_{10}O_4Li_2$: C, 52.21; H, 5.48%. Na(3-BA–MA) Found: C, 44.3; H, 4.6. Calc. for $C_8H_{10}O_4Na_2$: C, 44.45; H, 4.66%. K(3-BA–MA) Found: C, 38.5; H, 4.0. Calc. for $C_8H_{10}O_4K_2$: C, 38.69; H, 4.06%. Mg(3-BA–MA)·$\frac{1}{2}H_2O$ Found: C, 46.9; H, 5.4. Calc. for $C_{16}H_{22}O_9Mg_2$: C, 47.22; H, 5.45%. Ca(3-BA–MA)·$\frac{1}{2}H_2O$ Found: C, 44.1; H, 4.8. Calc. for $C_{16}H_{22}O_9Ca_2$: C, 43.82; H, 5.06%. Sr(3-BA–MA)·$\frac{1}{2}H_2O$ Found: C, 36.0; H, 3.8. $C_{16}H_{22}O_9Sr_2$: C, 36.01; H, 4.17%.

Ba(3-BA–MA) Found: C, 31.3; H, 3.3. Calc. for $C_8H_{10}O_4Ba$: C, 31.25; H, 3.28%. Li(3-BA–AA) Found: C, 49.4; H, 4.8. Calc. for $C_7H_8O_4Li_2$: C, 49.44; H, 4.74%. Na(3-BA–AA) Found: C, 41.45; H, 3.9. Calc. for $C_7H_8O_4Na_2$: C, 41.59; H, 3.99%. K(3-BA–AA)·½H_2O Found: C, 34.6; H, 3.4. Calc. for $C_{14}H_{18}O_9K_4$: C, 34.55; H, 3.73%. Mg(3-BA–AA)·½H_2O Found: C, 44.8; H, 4.4. Calc. for $C_{14}H_{18}O_9Mg_2$: C, 44.38; H, 4.79%. Ca(3-BA–AA) Found: C, 42.0; H, 4.15. Calc. for $C_7H_8O_4Ca$: C, 42.85; H, 4.11%. Sr(3-BA–AA)·½H_2O Found: C, 33.3; H, 3.25. Calc. for $C_{14}H_{18}O_9Sr$: C, 33.26; H, 3.59%. Ba(3-BA–AA) Found: C, 28.9; H, 2.8. Calc. for $C_7H_8O_4Ba$: C, 28.65; H, 2.75%.

Thermal reaction

The monomeric salt (1.5 g) was put into a Pyrex tube, and heated in an oil bath under reduced pressure at 200–250 °C for 2 h. The reaction mixture was dissolved in water, acidified with hydrochloric acid, and then extracted with diethyl ether. The extracts were treated with diazomethane in diethyl ether. The methyl ester derivatives of the products were analysed by gas chromatography using dimethyl succinate as an internal standard.

Isolation and spectroscopic analysis

Equimolar K(3-BA–MA) (57.9 g) was heated at 225 °C for 2.5 h and subsequently treated as described above. Distillation of the crude methyl ester (110–112 °C/6.5 mmHg) gave 14.1 g of dimethyl (*E*)-hex-1-ene-1,5-dicarboxylate (dimethyl ester of **4**); *m*/*z* 201 (MH); δ_H(400 MHz; $CDCl_3$) 1.17 (3 H, d), 1.56 (1 H, m), 1.84 (1 H, m), 2.22 (2 H, q), 2.45 (1 H, m), 3.68 (3 H, s), 3.70 (3 H, s), 5.85 (1 H, d, *J* 15.67), 6.96 (3 H, dt, *J* 15.67); δ_C(125 MHz; $CDCl_3$) 17.01 (CH_3), 29.80 (CH_2), 31.86 (CH_2), 38.77 (CH), 51.46 (OCH_3), 51.65 (OCH_3), 121.52 (=CH), 148.29 (=CH), 168.98 (C=O) and 172.62 (C=O); ν_{max}(NaCl, neat)/cm^{-1} 1658 (C=C) and 1726 (C=O).

Equimolar K(3-BA–AA) (55.3 g) was heated at 200 °C for 2 h and subsequently treated as described above. Distillation of the crude methyl ester (83–84 °C/1.5 mmHg) gave 22.3 g of dimethyl (*E*)-pent-1-ene-1,5-dicarboxylate (dimethyl ester of **5**); *m*/*z* 187 (MH); δ_H(400 MHz; $CDCl_3$) 1.81 (2 H, m), 2.26 (2 H, q), 2.35 (2 H, t), 3.68 (3 H, s), 3.73 (3 H, s), 5.85 (1 H, d, *J* 15.70), 6.94 (1 H, dt, *J* 15.70); δ_C(125 MHz; $CDCl_3$) 23.19 (CH_2), 31.38 (CH_2), 33.19 (CH_2), 51.47 (OCH_3), 51.62 (OCH_3), 121.74 (=CH), 148.05 (=CH), 166.93 (C=O) and 173.52 (C=O); ν_{max}(NaCl, neat)/cm^{-1} 1658 (C=C) and 1728 (C=O).

Results and discussion

Preparation of the monomeric salts

The monomeric salts were prepared by neutralizing a binary acid solution with aqueous metal hydroxide, and then drying under reduced pressure at 60 °C. The elemental analysis of Ca(3-BA–AA) did not agree with the calculated value due to high hygroscopicity. Some binary salts had 0.5 mol water of crystallization. However, because the reaction was carried out at a high temperature (200–220 °C) as well as under reduced pressure, it is considered that the water was removed initially and did not affect the reaction. Thermoanalytical measurement by means of DSC was carried out. In the samples containing water of crystallization, the peaks due to the elimination of water were found (*ca.* 100 °C). In all the salts, endothermic peaks were not found from 100 to 220 °C. This suggests that the salts do not melt below 220 °C.

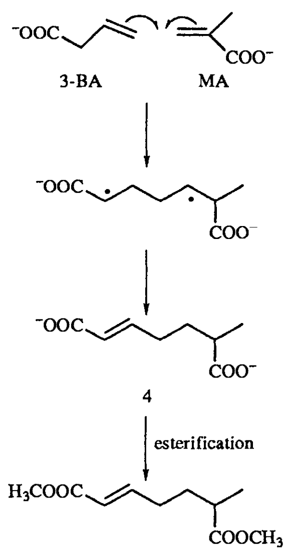
Thermal reactions of salts of (3-BA–MA)

Thermal reactions of the binary salts of an equimolar mixture were performed at 200 °C for 2 h. The products were acidified and subsequently converted to the methyl esters using diazomethane. The gas chromatograms of the esters obtained from Na(3-BA–MA) showed four peaks. The first and second peaks were those of methyl esters of dimers of MA. The first peak corresponded to dimethyl 4-methylpent-1-ene-2,4-dicarboxylate[1] (dimethyl ester of **1**) and the second peak corresponded to dimethyl hex-1-ene-2,5-dicarboxylate[2] (dimethyl ester of **2**) as shown by the co-injection method. The third peak corresponded to dimethyl (*E*)-hex-1-ene-1,6-dicarboxylate[11,12] (dimethyl ester of **3**) as the methyl ester of 3-BA dimer. The product corresponding to the fourth peak was isolated by distillation under reduced pressure after esterification and identified by ^1H NMR, ^{13}C NMR, mass and IR spectroscopy as dimethyl (*E*)-hex-1-ene-1,5-dicarboxylate (dimethyl ester of **4**) which is a methyl ester of the novel cross-coupled dimer of 3-BA with MA. The conversions of these dimers were determined by GC using dimethyl succinate as an internal standard after esterification. The results are summarized in Table 1.

Table 1 Dimer conversion of binary salts of 3-BA–MA

Salt	*T*/°C	*t*/h	Conversion (%)[a] 1	2	3	4
Li	200	2	n.r.[b]			
Na	200	2	2.6	4.0	2.8	22.2
K	200	2	—	—	2.9	28.0
K	230	2	1.6	—	6.4	62.2
K	250	2	5.2	—	8.3	59.7
Mg	200	2	—	6.0	—	7.1
Ca	200	2	—	13.2	—	5.5
Sr	200	2	—	12.4	—	7.2
Ba	200	2	—	13.2	—	—

[a] Determined by GC after esterification. [b] No reaction.



These reactions did not cause the rearrangement of 3-BA into crotonic acid which occurred in the thermal reaction of salts of 3-BA. This suggests that, in the solid-state reaction, the dimerization occurred prior to the rearrangement. The lithium salt did not react under these conditions. The low reactivity of Li(3-BA–MA) may be due to an unfavourable molecular arrangement of the monomeric salts in the crystal lattice, which makes it difficult for Li(3-BA–MA) to produce dimers. From the alkaline earth salts, the MA dimer **2** and cross-coupled dimer **4** were obtained, but these conversions occurred in low yields. From K(3-BA–MA), the 3-BA dimer **3** and cross-coupled dimer **4** were produced. We previously reported that the formation of **2** occurs with the destruction of the crystal structure of the monomeric salt in the thermal reaction, while in the formation of **1** the crystal state is retained as the reaction proceeds.[1–5] During the formation of 3-BA dimer **3** the crystal state was found to be maintained as the dimerization

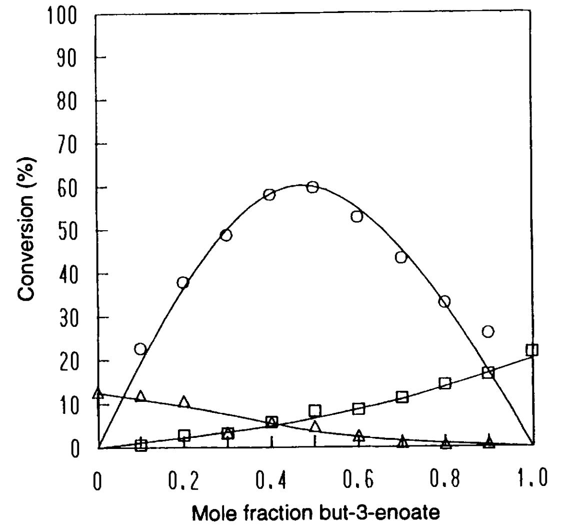


Fig. 1 Conversion of potassium but-3-enoate–methacrylate into dimers at 250 °C for 2 h; △, **1**; □, **3**; ○, **4**

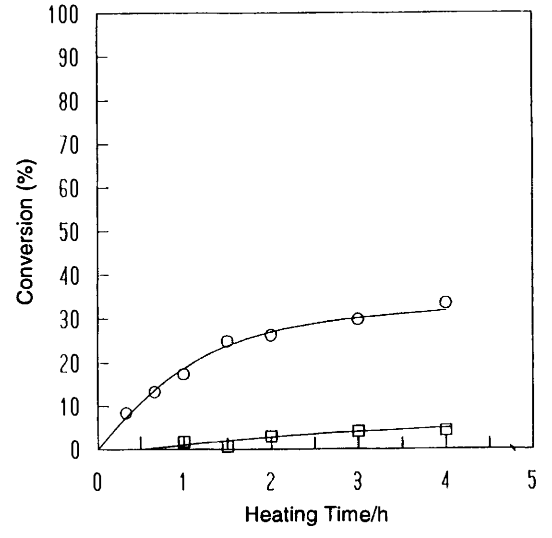
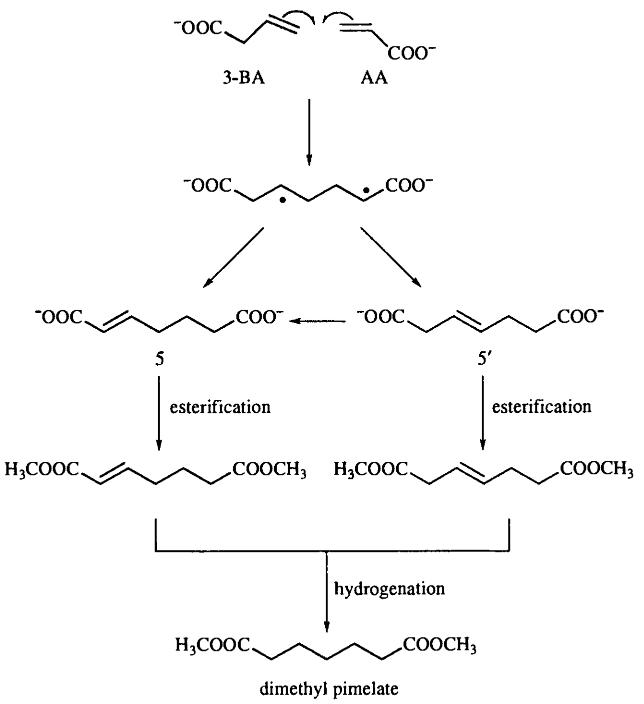


Fig. 2 Conversion of potassium but-3-enoate–methacrylate into dimers at 200 °C; □, **3**; ○, **4**

proceeds.[11,12] These results suggest that with alkaline earth salts the crystal state of the reaction system was destroyed to become amorphous as the thermal reaction proceeded, while the crystal state was maintained in the potassium salt. It could be that the destruction of the crystal structure of the alkaline earth salts in the thermal reaction causes the difficulties in the reaction of 3-BA with MA. The thermal reaction of the potassium salt, which showed the highest conversion into cross-coupled dimer **4** in the binary equimolar salts used, was further investigated.

When the reaction temperature was increased to 230 or 250 °C, the conversion of equimolar K(3-BA–MA) into **4** increased to *ca.* 60%. The conversion into dimers at 250 °C is shown as a function of the composition of K(3-BA–MA) in Fig. 1; the highest conversion into **4** was obtained using the equimolar salts. The conversion of binary equimolar potassium salts into dimers at 200 °C *versus* time is shown in Fig. 2. The conversion into **4** increased with time, and reached 33.4% after 4 h. The formation of the trimer was not seen even after 4 h. The X-ray diffraction pattern of equimolar K(3-BA–MA) indicated a crystalline salt, which was different from the individual patterns of potassium but-3-enoate and potassium methacrylate. This suggested equimolar K(3-BA–MA) has a new crystal phase different from that of the individual salts. Moreover, the diffraction peaks shifted slightly, maintaining the crystal state, as the



dimerization proceeded. The initial peaks of the monomeric salt at 2θ = 27.60°, 29.40° and 34.70° slightly shifted to 27.98°, 29.50° and 35.13°, respectively, on 33.4% dimer formation. This indicates the formation of solid solution crystals between the monomeric salts and the dimeric salt produced. In the solid state thermal reaction of the binary salts of crotonic acid–MA, it was found that the formation of solid solution crystals controls the selectivity of the product of dimerization.[9,10]

We previously reported that the thermal reaction of alkali methacrylates in the solid state gave a polymer having high molecular weight (388 000–480 000 u).[6] In contrast, potassium but-3-enoate was found to give oligomers with the rearrangement of but-3-enoic acid to crotonic acid.[11] However, the thermal reaction of binary K(3-BA–MA) gave the cross-coupled dimer selectively without any rearrangement of 3-BA because of the formation of a new crystal phase of the monomeric binary salts and the formation of solid solution crystals during dimerization.

Thermal reactions of salts of (3-BA–AA)

Thermal reactions of the binary salts of an equimolar mixture were performed similarly to the thermal reactions of salts of 3-BA–MA at 200 °C for 2 h. The gas chromatograms of the esterified products obtained from Na(3-BA–AA) showed three peaks. The first peak corresponded to that of the methyl ester of 3-BA dimer, dimethyl (*E*)-hex-1-ene-1,6-dicarboxylate (dimethyl ester of **3**), as shown by the co-injection method. The product corresponding to the second peak was separated by distillation under reduced pressure and identified by ^{1}H NMR, ^{13}C NMR, mass and IR spectroscopy as dimethyl (*E*)-pent-1-ene-1,5-dicarboxylate (dimethyl ester of **5**) which is a methyl ester of the novel cross-coupled dimer of 3-BA with AA. The product corresponding to the third peak could not be isolated by distillation because of thermal instability, but it was proposed that the product was dimethyl (*E*)-pent-2-ene-1,5-dicarboxylate (dimethyl ester of **5′**) as the isomer of **5**. This was tested by the hydrogenation of the combined mixture of **5** with **5′** which produced dimethyl pimelate (heptanedioate) quantitatively, identified by spectroscopic data. The results are summarized in Table 2.

These reactions did not cause the rearrangement of 3-BA into crotonic acid. The lithium salts did not react under these conditions. In all the other salts, the formation of 3-BA dimer **3** was slight (below 1%) or did not occur, and the cross-coupled

Table 2 Dimer conversion of binary salts of 3-BA–AA

Salts	T/°C	t/h	Conversion (%)[a] 3	5′	5	5 + 5′
Li	200	2	n.r.[b]			
Na	200	2	1.0	13.3	34.5	47.8
K	200	2	Trace	13.1	37.5	50.6
K	230	2	Trace	11.7	47.0	58.7
Mg	200	2	—	1.9	3.5	5.4
Ca	200	2	—	3.7	6.0	9.7
Sr	200	2	—	4.8	2.9	7.7
Ba	200	2	—	4.4	3.1	7.5

[a] Determined by GC after esterification. [b] No reaction.

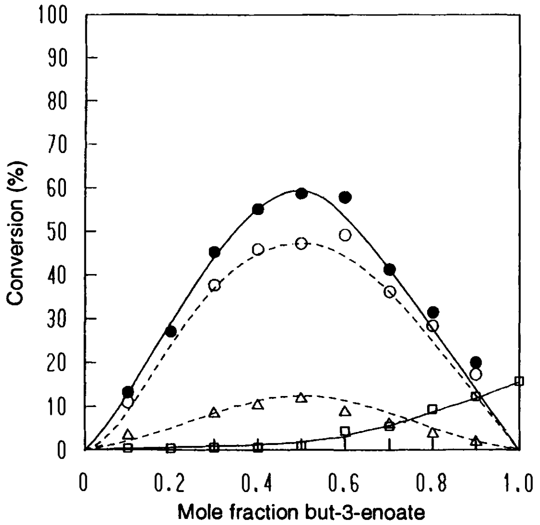


Fig. 3 Conversion of potassium but-3-enoate–acrylate into dimers at 230 °C for 2 h; □, 3; ○, 5; △, 5′; ●, 5 + 5′

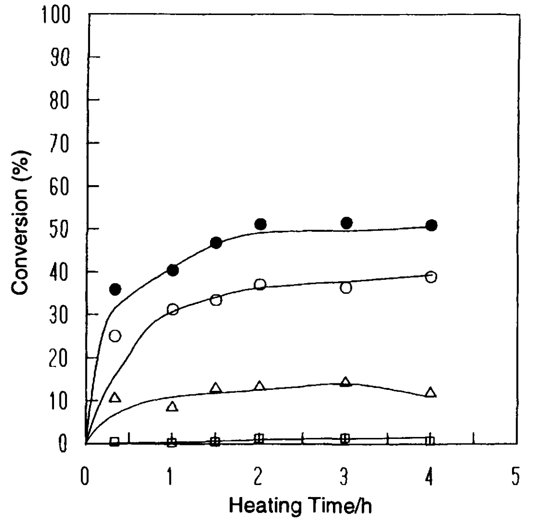


Fig. 4 Conversion of potassium but-3-enoate–acrylate into dimers at 200 °C; □, 3; ○, 5; △, 5′; ●, 5 + 5′

dimerization occurred virtually selectively. The total conversions of the alkaline earth salts (5.4–9.7%) were lower than those of the sodium and potassium salts (47.8–50.6%). The lower conversions of alkaline earth salts were attributed to the destruction of the crystal structure of monomeric salts in the thermal reaction. The thermal reaction of the potassium salts was further investigated.

When the reaction temperature was raised to 230 °C, the combined conversion of equimolar K(3-BA–AA) into **5** and **5′** increased to 58.7%. The conversions into dimers at 230 °C are shown as functions of the composition of K(3-BA–AA) in Fig. 3. The combined conversion into **5** and **5′** was the highest with the equimolar salts. The conversions of equimolar K(3-BA–AA) into dimers *versus* time at 200 °C are shown in Fig. 4. No formation of the trimer was seen even after 4 h. The conversion into **5** increased with time and reached 39.0% after 4 h. The conversion into **5′** also increased with time after 3 h (14.6%), but then decreased and reached 11.7% after 4 h. This decrease was due to a hydrogen transfer reaction of unstable **5′** into **5**. The X-ray diffraction pattern of the equimolar K(3-BA–AA) indicated a crystalline salt suggesting a new crystal phase of equimolar K(3-BA–AA) different from a mixture of K3-BA and KAA. The diffraction peaks shifted slightly, maintaining the crystal state, as the dimerization proceeded. The initial peaks of monomeric salts at 2θ = 22.08°, 29.55° and 37.15° slightly shifted to 21.98°, 29.39° and 36.88°, respectively, on 24.3% dimer formation. This suggested, similar to K(3-BA–MA), the formation of solid solution crystals between the monomeric salts K(3-BA–AA) and the produced dimeric salts.

Previously we found that the thermal reaction of alkali and alkaline earth acrylates in the solid state produced cross-linked polymers.[13] We have now shown that the thermal reactions of K(3-BA–MA) and K(3-BA–AA) gave cross-coupled dimers without cross-linking and that the rearrangement was due to the formation of new crystals of the monomeric binary salts and of solid solution crystals as the dimerization proceeded.

Conclusions

It is concluded that a new crystal phase is formed with monomeric equimolar K(3-BA–MA) or K(3-BA–AA) which differs from that of the individual salts. In addition, the formation of solid solution crystals between monomeric salts and the dimeric salts produced from the reaction induced selective cross-coupled dimerization without rearrangement of but-3-enoic acid to crotonic acid.

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