Synthesis and Rapid Polymerizations of Aryl- and Alkyl-bis(azetidine-2,4-dione)s to Polymalonamide Elastomers

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ABSTRACT: Two new synthetic methodologies for making aryl- and alkyl-bis(azetidine-2,4-dione)s have been accomplished in this study. A new family of *N*,*N*′-benzophenonyl bis(azetidine-2,4-dione)s (2) has been successfully synthesized through autoxidation of readily available diphenylmethane bis(azetidine2,4-dione)s (1) in 70−80% yields. In addition, the synthesis of *N*,*N*′-alkylene bis(azetidine-2,4-dione)s (3) was accomplished through sensitized photocyclization of *N*,*N*′-alkylene bis(*N*-formyl-2-methylacrylamide)s in a new three-step process from alkylene diamines in overall yields of 63−80%. The prepared bis(azetidine-2,4-dione)s were converted to polymalonamide elastomers in two steps by reacting first with a long-chained polyether diamine of 2000 g·mol^{-1} molecular weight to form the prepolymers. Subsequently, the prepolymers were melt-polymerized with hexamethylene diamine to produce the final elastomeric polymalonamides. The present study further investigated the reactivities of these aryl- and alkyl-bis(azetidine-2,4-dione)s as well as their elastomeric property differences due to structural variations. The study found that the order of the intermediate's reactivity toward amines is (2) > (1) > (3). This implies that aryl azetidine-2,4-diones, (1) and (2), are more reactive than their aliphatic counterpart (3) toward amines in their ring-opening reactions. Furthermore, the ketone-conjugated aromatic intermediates (2) were found to produce the highest molecular weight polymalonamides in short reaction time and result in polymalonamides with overall superior mechanical properties. For the final elastomeric polymalonamides produced, we found that aromatic polymalonamides were mostly amorphous, but aliphatic elastomeric polymalonamides were fibrous semicrystalline. All of the polymalonamides based on aryl bis(azetidine-2,4-dione)s possess temperature-resistant properties of >350 °C. The study indicated that the carbonyl activated bis(azetidine-2,4-dione)s, such as (2), can serve as the best candidate intermediates for making elastomeric polyamides via the rapid reaction injection molding (RIM) process similar to those practiced in polyurethanes.

Introduction

In our previous papers[1−7] on bis(azetidine-2,4-dione) chemistry, we reported syntheses and facile ring-opening reactions of diphenylmethane bis(azetidine2,4-dione)s (1).[6] Whereas a preliminary one-shot melt polymerization of (1) with alkylene diamines has been successful, unsatisfactory molecular weight build up of polymalonamides was found to be an area needing improvement. To search for bis(azetidine-2,4-dione) intermediates that are better than those previously reported, our present study has synthesized a new series of bis(azetidine-2,4-dione)s with structural variations. Specifically, we synthesized a new aliphatic series and a benzophenonyl series to complement the original series (1). Our major focus was to correlate reactivity−structure relationships and thereby identify an optimum intermediate. In addition, we were also interested in finding out the influence of different polymer-chain structures on the performance of the final product, elastomeric polymalonamides.

Because diphenylmethane bis(azetidine2,4-dione)s (1) could be easily prepared from MDI and ketenes through a one-step cycloaddition, our approach to benzophenyl bis(azetidine-2,4-dione)s was based on an air oxidation of the methylene group. Although the conversion of diphenylmethanes to benzophenones via autoxidation and base-catalyzed oxidation was well known as early as 1965,[8] there has been little literature concerning the methylene-bridge oxidation where diarylmethanes are functionalized with amine-containing derivatives. So far, there is only one report[9] by Park and Hamilton that discusses an amino-substituted fluorene oxidized to an amino fluoren-9-one without oxidation of the amino group using cesium carbonate as the oxidizing reagent. To our knowledge, no *N*,*N*′-diphenylmethane imides have been autoxidized with oxygen to *N*,*N*′-benzophenonyl imides. Because we failed to affect the autoxidation or oxidation of (1) under the base condition as described in the literature procedures, we carried out autoxidation of (1) directly and attempted to oxidize the methylene bridge of (1) to a carbonyl-group. Caruso[10] did the autoxidation of hydrocarbons at a benzylic position and found that it produced acid products under a duo-catalyst system of $Mn(OAc)_2$ and $Co(OAc)_2$. We modified the Caruso procedure by carrying out oxidation under a milder condition of 90−100 °C, thereby preventing overoxidation.

For a comparative study, we additionally investigated the synthesis of aliphatic bis(azetidine-2,4-dione)s. Martin[11] in 1971 indicated that aliphatic azetidine-2,4-diones synthesized by a thermal cycloaddition between ketene and aliphatic isocyanate was not efficient. Our trials confirmed the low reactivity of aliphatic isocyanates; therefore, the one-step cycloaddition route was abandoned. Because of this low reactivity shortcoming, we searched for an alternative synthetic approach. In 1979, Maruyama[12,13] reported an interesting route for synthesizing high-yield *N*-alkyl azetidine-2,4-diones using a photochemical process. We have developed this photochemistry to produce *N*,*N*′-alkylene bis(azetidine-2,4-dione)s by using readily available chemicals beginning with alkylene diamines.

Finally, the reactivity of three structurally different intermediates was monitored during their reactions with amine as well as during the melt polymerization. Preliminary structure−property relationships of the resulting elastomeric polymalonamides were also explored in this study.

Experimental Section

Materials. 4,4′-Methylene-diphenylene diisocyanate (4,4′-MDI), sodium bromide (NaBr), cobalt acetate [$Co(OAc)_2$], manganese

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acetate [$Mn(OAc)_2$], and dicumyl peroxide, each with >99% purity, were purchased from Aldrich. 1,1′-(Methylene-1,4′-diphenylene)bismaleimide with 95% assay was also purchased from Aldrich; 99% purity of 2-ethylbutyryl chloride and formic acid were supplied by Acros and methacryloyl chloride with 97% purity and hexamethylene diamine with 98% purity were bought from Lancaster. ACS grades of triethylamine, ethylene diamine, toluene, xylenes, methanol, cyclohexane, acetone, and *N*,*N*-dimethyl formamide (DMF) were all obtained from Tedia. Oxypropylene-based polyether diamine (Jeffamine D2000) with a connecting secondary carbon amine on the chain's terminal position was a BASF product.

Measurements. NMR and FTIR spectra of all synthesized intermediates were recorded on a Varian Gemini-200 FT-NMR spectrometer and a Perkin-Elmer Spectrum One Fourier transfer infrared spectrometer, respectively. Elemental CHN analysis was performed on a Heraeus CHN-OS rapid analyzer, whereas electron ionization mass (EIMS) analysis was performed on a ThermoQuest MAT 95XL apparatus. We prepared the films of polymalonamides by casting their DMF solutions on a Teflon mold, followed by drying at 60 °C in an oven for 48 h and additional drying in a high vacuum oven at room temperature for 2 h prior to carrying out the tensile testing and DSC measurements. Their mechanical behaviors were measured by HT-8504 (Hung Ta Instrument, Taiwan) with a crosshead speed of 100 mm/min at room temperature. The DSC measurement was performed using a Seiko SII model SSC/5200 at a heating and cooling rate of 10 °C/min in N_2. The secondary heating curves of DSC were also obtained and recorded. TGA was carried out on a Seiko SII model SSC/5200 at a heating rate of 10 °C/min in N_2.

Synthesis of *N*,*N*′-Benzophenonyl Bis(azetidine-2,4-dione)s (2)a−d by Autoxidation of (1)a−d. A general procedure for preparing *N*,*N*′-benzophenonyl bis(azetidine-2,4-dione)s (2) via autoxidation of (1) is described below. The synthesis of 1,1′-(4,4′-carbonylbis(1,4′-phenylene))bis(3,3-diethylazetidine-2,4-dione) (2)b from autoxidation of intermediate (1)b was performed as follows.

The autoxidation[10] of intermediate (1)b was conducted in a three-necked round-bottomed Pyrex-reaction flask equipped with a magnetic stirrer, a gas dispersion fritted disk, a snake-shaped condenser, and a thermometer under a dried oxygen atmosphere. Intermediate (1)b (5.00 g, 11 mmol) was mixed with 50 mg (1 wt % of intermediate (1)b) each of NaBr, $Co(OAc)_2$, and $Mn(OAc)_2$ and with 100 mg (2 wt % with respect to that of intermediate (1)b) of dicumyl peroxide in 50 mL of acetic acid. Oxygen was introduced to the solution through a fritted disk. The solution was stirred by a magnetic stirrer at a temperature controlled within the range of 95−100 °C. During a 12 h period, the complete disappearance of intermediate (1)b was observed by TLC. In the meantime, the appearance of a new absorption at 1659 cm^{-1} of the benzophenonyl carbonyl group was readily detected by FTIR. By distilling off acetic acid, the crude product was isolated as a solid mess. Further purification by recrystallization with 50/25 mL (2/1 v/v) acetone/methanol solution gave a white crystal intermediate (2)b (4.13 g, 80%) with a melting point of 115 to 116 °C.

1,1′-(4,4′-Carbonylbis(4,1-phenylene))bis(3,3-dimethylazetidine-2,4-dione) (2)a. Yield = 70%. mp = 199 to 200 °C. ^{1}H NMR (δ, $CDCl_3$): 1.53 (s, 12H, $-CH_3$), 7.82 (d, 4H, Ar−H), 7.97 (d, 4H, Ar−H). Anal. Calcd: C, 68.31; H, 4.98; N, 6.93. Found: C, 69.04; H, 5.15; N, 7.18. EIMS: Calcd, 404; Found, 404.

1,1′-(4,4′-Carbonylbis(4,1-phenylene))bis(3,3-diethylazetidine-2,4-dione) (2)b. Yield = 80%. mp = 115 to 116 °C. ^{1}H NMR (δ, $CDCl_3$): 1.10 (t, 12H, $-CH_3$), 1.84 (q, 8H, $-CH_2-$), 7.83 (d, 4H, Ar−H), 7.99 (d, 4H, Ar−H). Anal. Calcd: C, 70.42; H, 6.13; N, 6.08. Found: C, 71.05; H, 6.15; N, 6.21. EIMS: Calcd, 460; Found, 460.

1,1′-(4,4′-Carbonylbis(4,1-phenylene))bis(3-ethyl-3-butylazetidine-2,4-dione) (2)c. Yield = 80%. mp = 94−96 °C. ^{1}H NMR (δ, $CDCl_3$): 0.91 (t, 6H, $-CH_3$), 1.05 (t, 6H, $-CH_3$), 1.40 (m, 8H, $-CH_2-$), 1.79 (m, 8H, $-CH_2-$), 7.83 (d, 4H, Ar−H), 7.98 (d, 4 h, Ar−H). Anal. Calcd: C, 72.07; H, 7.02; N, 5.24. Found: C, 72.25; H, 7.52; N, 5.35. EIMS: Calcd, 516; Found, 516.

4,4′-Bismaleimidobenzophenone (2)d. Yield = 40%. mp = 201 to 202 °C (ref: 226 to 227 °C). ^{1}H NMR (δ, DMSO-d_6): 7.23 (s, 4H, −CH=CH−), 7.55 (d, 4H, Ar−H), 7.86 (d, 4H, Ar−H). Anal. Calcd: C, 67.74; H, 3.25; N, 7.52. Found: C, 67.38; H, 3.27; N, 7.48. EIMS: Calcd, 372; Found, 372.

Photosynthesis of *N*,*N*′-Alkylene Bis(azetidine-2,4-dione)s (3)a−c. Photocyclization reactions were carried out to synthesize *N*,*N*′-alkylene bis(azetidine-2,4-dione) intermediates, (3)a−c. These alternative syntheses were investigated because cycloaddition between aliphatic isocyanates and ketenes results in low yields of products (∼20%). A general three-step procedure of preparing *N*,*N*′-alkylene bis(azetidine-2,4-dione)s (3) is described below. Synthesis of *N*,*N*′-hexamethylene-1,6-bis(3,3-dimethylazetidine-2,4-dione) (3)b is exemplified as follows.

Preparation of N,N′-Hexamethylene-1,6-bisformamide (3)b-2. Hexamethylene diamine (34.90 g, 0.3 mol) weighed in a two-necked round-bottomed flask equipped with a Dean−Stark trap was dissolved with 250 mL of dried toluene. Formic acid (55.20 g, 1.2 mol) was slowly added to the solution at room temperature under a dried nitrogen atmosphere. The combined mixtures were heated and stirred to reflux to remove the water produced from the condensation reaction. The formation of the formamide was observed by FTIR monitoring with the appearance of C=O and N−H absorptions at 1630, 1646, and 3274 cm^{-1}, respectively. After 9 h of reaction time, formation of water ceased, and the mixture was cooled to room temperature. Then, solid product precipitated. After filtration of the solid precipitate, 50.50 g of white solid intermediates (3)b-2 was obtained in 98% yield. The melting point of the product was 106 to 107 °C.

Preparation of N,N′-Hexamethylene-1,6-bis(N-formyl-2-methylacrylamide) (3)b-3. Compound (3)b-2 (17.20 g, 0.1 mol) and 25.30 g (0.25 mol) of triethylamine were added to a three-necked round-bottomed flask containing 150 mL of dried toluene. To this solution was added a mixture of 25.10 g (0.24 mol) of methacryloyl chloride in 50 mL of dried toluene dropwise at room temperature over 50 min. After the completion of the dropwise addition, the solution was stirred for another 20 h until the carbonyl absorption of compound (3)b-2 at 1630 cm^{-1} completely disappeared. The formation of the new product had characteristic FTIR absorptions at 1660 and 1720 cm^{-1}. After filtration of the salt and vacuum evaporation of the product solution, compound (3)b-3 was obtained as crude product, which was directly used in the subsequent photosynthetic steps. (Note: The pure compound (3)b-2 can be purified and isolated as low-melting crystals (mp = 34 °C), but purification in this stage would suffer a great loss of materials in the isolation process.)

Preparation of N,N′-Hexamethylene-1,6-bis(3,3-dimethylazetidine-2,4-dione) (3)b. The crude compound (3)b-3 (∼29 g) was dissolved in 800 mL of acetone. Photocyclization was performed with a 27 W Hg lamp at room temperature in a photoreactor with stirring. After 7 h of photolysis, the completion of the photochemical transformation was observed on the basis of FTIR monitoring. The disappearance of 1665 cm^{-1} of double-bond absorption was accompanied by the appearance of 1731 cm^{-1} of azetidine-2,4-dione absorption, and the FTIR monitoring was also confirmed by the disappearance of double bonds of (3)b-3 in NMR. A sticky product mixture (29.0 g) was obtained after using a rotary vacuum to evaporate the acetone. Subsequently, crystallization using cyclohexane yielded 25.0 g of high purity white crystalline solid intermediate (3)b.

***N*,*N*′-Ethylene-1,2-bis(3,3-dimethylazetidine-2,4-dione) (3)a.** Yield = 65% (for two step). mp = 131 to 132 °C. ^{1}H NMR (δ, $CDCl_3$): 1.20 (s, 6H, $-CH_3$), 3.30 (s, 4H, $-CH_2-$). Anal. Calcd: C, 57.13; H, 6.39; N, 11.10. Found: C, 56.34; H, 6.28; N, 10.62. FABMS: Calcd, 252.1; Found, 253.3.

***N*,*N*′-Hexamethylene-1,6-bis(3,3-dimethylazetidine-2,4-dione) (3)b.** Yield = 82% (for two step). mp = 103 to 104 °C. ^{1}H NMR (δ, $CDCl_3$): 1.37 (s, 16H, $-CH_2-$ and $-CH_3$), 1.63 (t, 4H, $-CH_2-$), 3.25 (t, 4H, N$-CH_2-$ and $-CH_2-$N). Anal. Calcd: C, 62.32; H,

7.84; N, 9.08. Found: C, 62.24; H, 7.66; N, 8.61. FABMS: Calcd, 308.17; Found, 309.5.

***N,N′*-Dodecamethylene-1,12-bis(3,3-dimethylazetidine-2,4-dione) (3)c.** Yield = 86% (for two step). mp = 97 to 98 °C. ^{1}H NMR (δ, $CDCl_3$): 1.26 (s, 16H, $-CH_2-$), 1.36 (s, 12H, $-CH_3$), 1.62 (t, 4H, $-CH_2-$), 3.24 (t, 4H, $N-CH_2-$ and $-CH_2-N$). Anal. Calcd: C, 67.32; H, 9.24; N, 7.14. Found: C, 67.17; H, 9.30; N, 6.85. FABMS: Calcd, 392.3; Found, 393.6.

Ring-Opening Reaction with *n*-Butylamine. A simple reactivity test for comparing different ring-opening reactions for the synthesized bis(azetidine-2,4-dione)s is described. Ring-opening of intermediate (1)b in $N^1,N^{1\prime}$-(4,4′-methylenebis(4,1-phenylene))bis(N^3-butyl-2,2-diethylmalonamide) (4) is exemplified as follows.

n-Butylamines (0.36 g, 4.9 mmole) were added to the solution of (1)b (1.00 g, 2.2 mmole), which was dissolved in 7 mL of dried DMF at room temperature with vigorous stirring. After 25 min under these conditions, a fully completed ring-opening reaction of (1)b was observed by TLC (ethyl acetate/*n*-hexane 1/4 v/v) and FTIR monitoring. The resulting solution was poured in 150 mL of water and was vigorously stirred for several hours. The white solid precipitate (compound (4), 1.29 g, 97%) was collected by filtration and dried by vacuum oven. The melting point of compound (4) was measured to be 193 to 194 °C.

***N*^{1},*N*$^{1\prime}$-(4,4′-Methylenebis(4,1-phenylene))bis(*N*^{3}-butyl-2,2-diethylmalonamide) (4).** Yield = 97%. mp = 193 to 194 °C. Reaction time: 25 min. ^{1}H NMR (δ, DMSO-d_6): 0.66 (t, 12H, $-CH_3$), 0.81 (t, 6H, $-CH_3$), 1.19−1.44 (m, 8H, $-CH_2CH_2-$), 1.86 (t, 8H, $-CH_2-$), 3.11 (d, 4H, $-CH_2-$), 3.82 (s, 2H, $Ar-H_2-Ar$), 7.09 (d, 4H, Ar−H), 7.47 (d, 4H, Ar−H), 8.09 (s, 2H, −NH−), 10.57 (s, 2H, −NH−). Anal. Calcd: C, 70.91; H, 8.84; N, 9.45. Found: C, 70.77; H, 8.88; N, 9.55. EIMS: Calcd, 592.4; Found, 592.6.

***N*^{1},*N*$^{1\prime}$-(4,4′-Carbonylbis(4,1-phenylene))bis(*N*^{3}-butyl-2,2-diethylmalonamide) (5).** Yield = 96%. mp = 164−166 °C. Reaction time: 68 s. ^{1}H NMR (δ, DMSO-d_6): 0.69 (t, 12H, $-CH_3$), 0.81 (t, 6H, $-CH_3$), 1.20−1.46 (m, 8H, $-CH_2CH_2-$), 1.90 (t, 8H, $-CH_2-$), 3.13 (d, 4H, $-CH_2-$), 7.67 (d, 4H, Ar−H), 7.79 (d, 4H, Ar−H), 8.06 (s, 2H, −NH−), 10.91 (s, 2H, −NH−). Anal. Calcd: C, 69.28; H, 8.31; N, 9.23. Found: C, 69.19; H, 8.13; N, 9.25. EIMS: Calcd, 606.4; Found, 606.6.

Synthesis of *N*^{1},*N*$^{1\prime}$-Hexamethylene-1,6-bis(*N*^{3}-butyl-2,2-dimethylmalonamide) (6). *n*-Butylamines (0.36 g, 4.9 mmole) were added to the solution containing intermediate (3)b (0.68 g, 2.2 mmole) in 5 mL of dried DMF at room temperature with stirring. The progress of the ring-opening reaction was monitored by ^{1}H NMR to observe the gradual disappearance of the chemical shift of triplet peaks (3.24 to 3.31 ppm) of the intermediate (3)b. It took 140 min for (3)b to disappear from the solution. The resulting solution was poured in 130 mL of water with agitation. White powders of compound (6) (0.82 g, 82%) were collected after filtration and drying at 60 °C by vacuum oven. The melting point of compound (6) was found to be 144 to 145 °C. (6): Yield = 82%. mp = 144 to 145 °C. Reaction time: 140 min. ^{1}H NMR (δ, DMSO-d_6): 0.80 (t, 6H, $-CH_3$), 1.25−1.35 (m, 28H, $-CH_2-$ and $-CH_3$), 3.01 (s, 8H, $-CH_2-$), 7.48 (s, 4H, −NH−). Anal. Calcd: C, 63.40; H, 10.20; N, 12.32, O 14.08. Found: C, 63.20; H, 10.05; N, 12.42, O 14.17. EIMS: Calcd, 454; Found, 454.

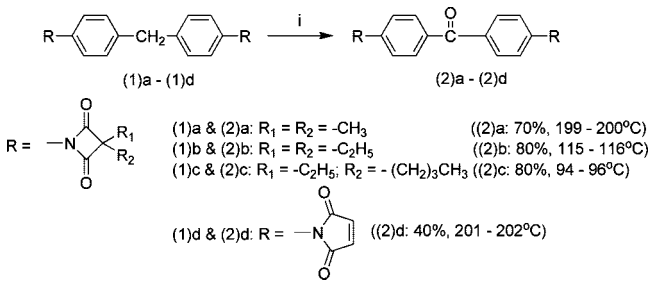
Preparation of Polymalonamide Elastomers. Elastomeric polymalonamides were synthesized from diamines and different bis(aztidine-2,4-dione) intermediates in a two-step process in the absence of any solvents. In the first step, bis(azetidine-2,4-dione)s reacted with a long-chained polyether diamine of 2 000 g·mol^{-1} molecular weight. Then, hexamethylene diamine was added to the resulting mixture to yield the final elastomeric polymers. The experiment details are summarized as follows: Bis(azetidine-2,4-dione), using intermediate (2)b as a demonstration (3.0 g, 6.5 mmole), was introduced to a round-bottomed reactor that was equipped with a mechanical stirrer. Then, bis(azetidine-2,4-dione)s and Jeffamine D2000 (4.2 g, 2.1 mmole) were added to the reaction flask. The mixture was vigorously stirred at 100 °C, and the progress of the prepolymer formation was monitored by GPC analysis until molecular weight ceased to increase in 30 min. Then, hexamethylene diamine (0.5 g, 4.4 mmole) was rapidly added at 60 °C. The resulting mixture was stirred, and the exothermic reaction was allowed to proceed without cooling. The polymer product became viscous and was accompanied by the phenomenon of rod-climbing. When the stirring stopped because of high viscosity, the mixture was cooled, and the time of reaction was recorded.

Results and Discussion

A method for synthesizing (1)a−c by 4,4′-MDI and ketene cycloaddition has been previously reported by J. C. Martin and has herein been modified.[6] In this report, six new bis(azetidine-2,4-dione) intermediates, (2)a−c and (3)a−c, were synthesized via new methodologies for the present study. All new synthesized intermediates were characterized by their melting points, FTIR, NMR, elementary analysis, and mass spectrum, as shown and discussed in the Experimental Section. In our approach, the autoxidation of the methylene group in the diphenylmethane structure of intermediates (1)a−d is known for its vulnerability for being attacked by oxygen and radicals.[14−16] This was carried out in our method as a means of making the benzophenonyl bis(azetidine-2,4-dione)s (2)a−d. The structural conversion was also designed to investigate the reactivity effects of azetidine-2,4-dione when an electron-withdrawing carbonyl group is introduced to the conjugated position of the dione's two phenyl rings. Although autoxidation of diphenylmethanes under either neutral or base-catalyzed conditions has been reported,[8] the conversion of their imide-protected derivatives to benzophenonyl moieties was unknown prior to our present work. In our study, several autoxidation conditions have been attempted using modified AMACO's autoxidation technology.[17] Our initial experiments focused on more severe autoxidation by carrying out the reaction in a PARR reactor at a temperature of ∼170 °C under high oxygen pressure of >200 psi. It was soon observed that methylene bridges of intermediate (1)a−d were overoxidized and resulted in the formation of carboxylic acid and other chain-cleaved derivatives as major products. In subsequent process modifications, autoxidation of intermediate (1)a−d was attempted at reflux temperature (138 °C) in an acetic anhydride solution under oxygen atmospheric pressure, but the desired benzophenonyl products were produced in only low yields, and several acetate derivatives were found to be the primary products.[18] On the basis of these observations, we further modified the autoxidation conditions by running autoxidation at a lower temperature of 95−100 °C in acetic acid. Under these milder conditions, intermediate (2)a−d with benzophenone moiety was found to be the primary product, as evidenced by the formation of a carbonyl absorption at 1659 cm^{-1} in FTIR and the disappearance of methylene protons of (1) at 3.97 ppm in chloroform-d_1. The products could be readily isolated by recrystallization after the concentrated crude products were treated with an acetone/methanol solution. The benzophenonyl bis(azetidine-2,4-dione)s (2) were isolated in yields of 70−80%. Furthermore, 4,4′-bismaleimidobenzophenone, a structurally related compound, was also obtained from a similar oxidation process from 4,4′-bismelaimidodiphenylmethane in 40% yield. Thus, it appears that this new autoxidation condition is applicable to converting the methylene group in diphenylmethane bis(azetidine-2,4-dione)s (1) to a carbonyl group for all imide-protected derivatives of diphenylmethanes.

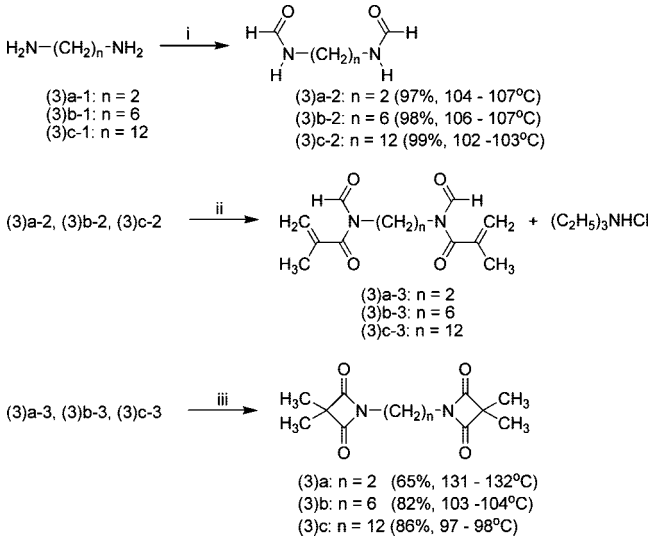
For the synthesis of the aliphatic bis(azetidine-2,4-dione) series, a different synthetic scheme was employed. The process requires three steps and involves a key photochemical cyclization step, which is shown in Scheme 2. This new approach was developed because no efficient cycloaddition route like the synthesis of aryl azetidine-2,4-diones through the ketene−isocyanate reaction has yet been achieved. In our investigation, only low yields (∼20%) of cycloadducts were found in all

Scheme 1. General Synthesis of *N,N′*-Benzophenonyl Bis(azetidine-2,4-dione)s (2)a−d via Autoxidation[a]



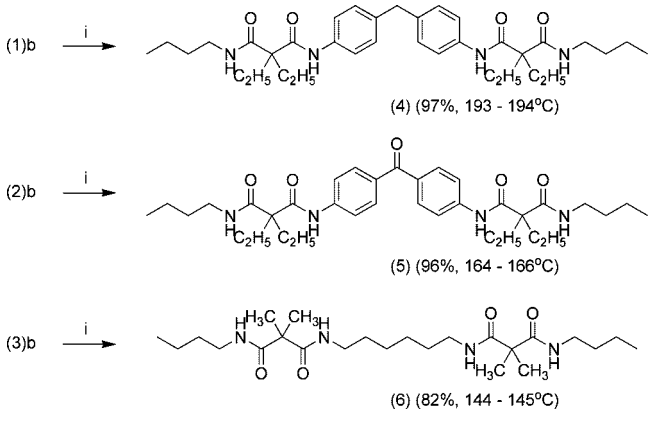
[a] (i) NaBr/$Co(OAc)_2$/$Mn(OAc)_2$/dicumyl peroxide, acetic acid, 95 °C.

Scheme 2. General Synthesis of *N,N′*-Alkylene Bis(azetidine-2,4-dione)s (3)a−c via Photochemistry[a]



[a] (i) Formic acid, toluene, reflux; (ii) methacryloyl chloride/triethylamine, toluene, room temperature; (iii) photocyclization, acetone.

Scheme 3. Ring-Opening Model Reaction for Azetidine-2,4-dione Activities of Diphenylmethane Type (1), Benzophenone Type (2), and Aliphatic Type (3)[a]



[a] (i) *n*-butylamine, DMF, room temperature.

ketene reactions involving aliphatic isocyanates. The new strategy for producing aliphatic bis(azetidine-2,4-dione)s (3) was based on the previous methodology of Maruyama and his coworkers.[12,13] Our synthetic path leads to the photoprecursor alkylene bis(*N*-formyl-2-methylacrylamide); however, we produce the photoprecursor in a much simpler and more straightforward manner. The starting raw materials are low-cost, readily available aliphatic diamines such as hexamethylene diamine, ethylene diamine, and dodecamethylene diamine. After the initial condensation with formic acid, the bisformamides formed were treated with methacryloyl chloride to give the photoprecursors. The precursors, alkylene bis(*N*-formyl-2-methylacrylamide)s, were then subjected to a photocyclization reaction using a high-pressure mercury lamp as the UV light source. We found that the addition of a triplet sensitizer such as xanthone is essential and can greatly accelerate the photoconversion. Acetone was also found to be a convenient solvent sensitizer capable of facilitating the conversion. The most efficient and optimal photoconditions were carried out at ambient temperature in a diluted acetone solution of approximately 0.12 M concentration. The conversion was completed in 7 h in >80% yield from the pure precursor. Another advantage of this photoconversion is that different UV light sources, even sunlight, could be used to affect the conversion. Moreover, the synthesis of aliphatic bis(azetidine-2,4-dione)s can be simplified by skipping the isolation of bis(*N*-formyl-2-methylacrylamide)s by directly photolyzing the crude precursors. This practice saved time as well as enhanced the overall yields for not losing bis(*N*-formyl-2-methylacrylamide)s in their isolation steps. For the three-step process, the overall yields from diamines were about 63−80%. All synthesized aliphatic bis(azetidine-2,4-dione)s (3)a−c were stable white crystalline solids.

For the melt polymerization producing polymalonamide elastomers, we carried out the preparation in a two-step process similar to the prepolymer process practice that is widely used in the synthesis of elastomeric polyurethanes (PU). In the first step, bis(azetidine-2,4-dione) intermediates were allowed to react with calculated amounts of a polyether diamine with an average molecular weight of about 2000 $g \cdot mol^{-1}$, Jeffamine D2000, to form azetidine-2,4-dione-terminated prepolymers. Because the reaction of the polyether diamine and bis(azetidine2,4-dione)s was slow, the mixtures were heated to about 100 °C while being mixed until all of the polyether diamine had been consumed, as determined by FTIR and GPC. In the second step of the polymerization, hexamethylene diamine was added to the prepolymers at 60 °C to form the elastomeric polymalonamides. The chain-extending reactions were rather rapid, and the final elastomers were generally formed in <5 min of stirring, as evident by the high built-up viscosities that eventually interrupted the stirring. Polymerization information from the representative runs and property data of polymalonamide elastomers are shown in Table 1. In our observations, we found that different reactivities of intermediates could be readily distinguished upon the addition of hexamethylene diamine within the duration of the polymerization time. The polymerization time in this study is defined as the stirring time at 60 °C upon the addition of the prepolymers with hexamethylene diamine. Termination of stirring is based upon the reaction itself when the viscosity of polymers prevents the stirring to continue.

On the basis of the data compiled in Table S1 with the recipes in the additional Supporting Information for all three bis(azetidine-2,4-dione)s, aliphatic bis(azetidine2,4-dione) (3)b was found to have the slowest polymerization rate with a polymerization time of 300 s with hexamethylene diamine. Benzophenonyl bis(azetidine-2,4-dione)s (2)b was the fastest with a polymerization time of only ~15 s. The reactivity of diphenylmethane intermediate (1)b had a reaction time of 150 s, and its reactivity lies between the previous two. The major reason for their differences is clearly due to the structural effect of the different substituents attached to azetidine-2,4-diones resulting in either an electron-donating or an electron-withdrawing effect. Among the three bis(azetidine-2,4-dione) intermediates, the

Scheme 4. Preparation of Polymalonamide Elastomers via Solvent-Free Prepolymer Polymerization

Table 1. Characterization of Polymalonamide Elastomers[a]

polymers	elongation %	strength MPa	M_n g·mol^{-1}	PD[b]	T_d °C[c]	T_m °C	T_g °C	HSC wt %[d]
I-45	354	0.9	25 188	1.48	353		−52	45
I-55	553	10.3	26 615	1.41	355		−56	55
I-65	151	8.4	26 615	1.34	358		−56	65
II-45	835	3.9	63 884	1.24	351		−53	45
II-55	432	15.7	57 435	1.92	351		−53	55
II-65	270	15.9	51 974	1.73	354		−55	65
III-45			20 207	1.42	306	149	−57	45

[a] I, II, and III series were made from the intermediates (1)b, (2)b and (3)b, respectively. [b] PD: polydispersity. [c] T_d: 5% weight loss. [d] HSC wt %: hard-segment content.

electron density of azetidine-2,4-dione groups in intermediate (2)b bearing benzophenonyl moiety is expected to be the lowest because of the double electron-withdrawing effects of the carbonyl and phenyl groups of benzophenones. The end result of this electron-withdrawing effect is the creation of an electron deficiency at the carbonyl carbon of bis(azetidine-2,4-dione)s, which makes them more susceptible to a nucleophilic attack. On the contrary, the azetidine-2,4-dione moieties in the aliphatic bis(azetidine-2,4-dione)s (3)b appear to be stabilized by electron-donating alkyl chains; therefore, the azetidine-2,4-diones in (3) are not activated by comparison.

In another reactivity study in solution, a similar reactivity trend has also been confirmed. In the experiment, each intermediate was allowed to mix with *n*-butylamine at room temperature in DMF solution. The molar ratio of *n*-butylamine to bis(azetidine-2,4-dione)s was fixed at 2.2, whereas the concentration of the solution was set at 0.3 M on the basis of bis(azetidine-2,4-dione)s. The TLC analysis of the mixture revealed that it takes 25 min at 25 °C for intermediate (1)b to complete the ring-opening reaction by *n*-butylamine but <68 s at 25 °C for intermediate (2)b to do the same. The reaction of intermediate (3)b with *n*-butylamine gave a malonamide derivative; however, it needed a whopping 140 min to complete. This result proves again that aromatic azetidine-2,4-diones are far more reactive than their alkylene counterparts such as intermediate (3)b, with the benzophenonyl intermediate (2)b as the most reactive among the intermediates studied.

The structural change in bis(azetidine-2,4-dione) intermediates also has impacted the resulting polymalonamide elastomer properties in several ways. Table 1 showed the thermal behaviors of these elastomers and their molecular weight analysis. The GPC analysis revealed that elastomer I-45−I-65, which was made from 1,1′-(4,4′-methylenebis(4,1-phenylene))bis(3,3-diethylazetidine-2,4-dione) (1)b, had a molecular weight of only 25 000−27 000 g·mol^{-1}, whereas, elastomer II-45−II-65, which was made from benzophenoyl series (2)b, had a molecular weight in the range of 52 000−64 000 g·mol^{-1}. The molecular weights of the elastomer II series are more than 2 times as large as those made from the aliphatic series. This implied that more reactive *N*,*N*′-benzophenonyl bis(azetidine-2,4-dione)s can readily build up to higher molecular weight polymers through a melt-polymerization process in short mixing times. The thermal stabilities of the elastomers analyzed on TGA revealed that aliphatic polymers exhibited T_d values of only slightly higher than 300 °C. However, T_d values of aryl polymalonamide elastomers were 351−358 °C and are much higher than those of the aliphatics (about 40−50 °C higher). Differential scanning calorimetry (DSC) analysis of all elastomers showed nearly the same glass-transition temperature (T_g) of −50 °C for their soft segments. There were no endothermal signals for the melt and hard-segment glass-transition temperature of aryl-polymalonamide elastomers, as observed on their DSC thermogram. On the contrary, the crystallization temperature and the melting enthalpy of alkyl elastomer III-45 were recorded at 62 and 149 °C, respectively, indicating that the aliphatic elastomeric polymalonamides are semicrystalline. Morever, an AFM study provided complemental evidence of fibrous material being observed in the topography of III-45 and aryl elastomers not being observed. The former are opaque in appearance, brittle in nature, and difficult for making good films for the mechanical tests. Amorphous aryl polymalonamide elastomers possessing either diphenylmethane or benzophenone structures are brown, tough polyamides that can be cast in film for mechanical strength measurements. Like the phenomenon that was generally observed in PU elastomers, mechanical strengths and elongations of polymalonamides are greatly influenced by their hard-segment and soft-segment ratios. With an increase in hard-segment contents, the strength of elastomers increases at the expense of elongation. Moreover, at the same hard-segment level, mechanical properties of elastomer II-65 (made from (2)b) perform much better than those of elastomer I-65 (made for (1)b). This result could be attributed to the benzophenonyl structure in polymalonamide as well as to their higher molecular weight. Interestingly, hard and soft segments of elastomer II-55 do not give any indication of segregation under our AFM examination. Instead, elastomer II-55 appears to be a completely phase-mixed material.

Conclusions

Two new synthetic methodologies for making aryl- and alkyl-bis(azetidine-2,4-dione)s have been accomplished in this study. The synthesis of *N*,*N*′-benzophenonyl bis(azetidine-2,4-dione)s was achieved by the autoxidation of their corresponding *N*,*N*′-diphenylmethane bis(azetidine-2,4-dione)s (1) at about 95−100 °C. The general synthesis of *N*,*N*′-alkylene bis(azetidine-2,4-dione)s (3) was accomplished by a photochemical route through the cyclization of alkylene bis(*N*-formyl-2-methylacrylamide) precursors. All of these polymeric intermediates can rapidly react with aliphatic diamines such as hexamethylene diamine in the formation of polymalonamides. In the two-step melt polymerization study of bis(azetineine-2,4-dione)s with polyether diamine and hexamethylene diamine, high-molecular-weight polymalonamide elastomers have been obtained at 60 °C in seconds. It was found that the activity of *N*,*N*′-benzophenonyl bis(azetidine-2,4-dione)s was the highest among the intermediates tested, whereas *N*,*N*′-alkylene bis(azetidine-2,4-dione)s seemed to have the lowest with *N*,*N*′-diphenylmethane bis(azetidine-2,4-dione)s being in between. This reactivity trend shown in azetidine-2,4-diones is parallel to that of polyisocyanate

intermediates, where aromatic isocyanates are more reactive than aliphatics. However, the stability of azetidine-2,4-diones in storage is superior to that of isocyanates. This research revealed that molecular weights of polymalonamide elastomers prepared by melt polymerization seem to be very dependent on the reactivity of the intermediates. Aryl polymalonamide elastomers were amorphous and aliphatic were semicrystalline, as indicated by DSC and AFM. The introduction of carbonyl groups to the aromatic ring conjugated to azetidine-2,4-dione greatly enhances the reactivity of azetidine-2,4-dione, showing an advantage in making superior polyamide elastomers through melt polymerization. Most significantly, the azetidine-2,4-dione chemistry carried out in this study offers an alternative approach for making elastomeric polyamide materials in a short mixing time and could have potential applications in the development of a new reaction injection molding (RIM) process for making polyamides.

Supporting Information Available: Recipes for polymalonamide elastomers and AFM images for the corresponding compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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