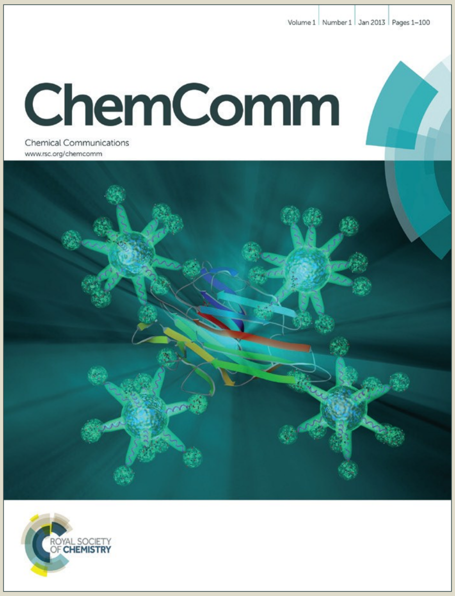
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Thermosetting resins with high fractions of free volume and inherent low dielectric constants

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This work demonstrates a new class of thermosetting resins, based on Meldrum's acid (MA) derivatives, which have high fractions of free volume and inherent low-k values of about 2.0 at 1 MHz. Thermal decomposition of the MA groups evolves CO_2 and acetone to create air-trapped cavities so as to reduce the dielectric constants.

Polymers are important materials in many fields of applications. The developments of new technologies urgently require advanced polymeric materials possessing high performance and critical properties. Although the polymer properties could be tailored and enhanced with physical blends, chemical modification, and formation of organic-inorganic hybrids with the existed polymers, developments of new polymers is still attractive, on both science and engineering viewpoints, to provide eye-catching materials for advanced applications.[1,2] For example, materials with low dielectric constant (low-*k*) are highly expected for advanced IC-technology nodes and high-frequency communication technologies. Herein, in this work we report a new class of thermosetting polymeric resins which have inherent low dielectric constants of about 2.0 at 1 MHz and good thermal and mechanical properties.

Preparation of monomers with designed chemical structures and specific chemical groups is a convenient and facile approach for property enhancements and functionalization of polymeric materials. In the case the specially-designed monomers are polymerized with a well-established synthesis route to result in the corresponding polymers. For example, thermosetting resins could be obtained with reaction of suitable monomers possessing specific functional groups such as epoxide, maleimide, isocyanate, benzoxazine, and benzocyclobutene etc. Furthermore, novel thermosetting resins which employ a new crosslinking reaction in the synthesis route are attractive, although in the case it is much more like developments of a new class of polymers and it usually takes much efforts and time. Aiming at this target, in this work the ketene-mediated addition reaction has been employed for the developments of a new class of thermosetting resins.

Ketenes have been used as monomers for preparation of polymers. Polyaddition of multifunctional ketenes with nucleophile-containing compounds, such as difunctional alcohols and amines, resulted in polyesters and polyamides.[3] Direct polymerization of ketenes was also performed to generate the corresponding linear polymers.[5] Nevertheless, the high reactivity of ketenes brings some limits for practical uses in polymer synthesis. To overcome this problem, uses of ketene precursors in polymer synthesis have been investigated. Yagci[6-8] utilized benzodioxinone as the precursors of ketenes for preparation of photo-induced crosslinked polymers. Hawker[9-13] used Meldrum's acid (MA) derivatives as ketene precursors and prepared MA-containing monomers and the corresponding liner polymers. The MA-possessing polymers could be self-crosslinked and post-functionalized with the ketene groups generated from the thermolytic reaction of the MA groups. Polyaddition reaction of bis-MA compounds with diols was also reported to result in linear polyesters.[14] Moreover, cyclobutanediol compounds, which could be used as bisphenol-A alternatives for synthesis of polyesters, were prepared from dimerization of MA derivatives and sequential reduction of the obtained MA-based dimers.[15]

In the literature, crosslinkable polymers possessing MA pendent groups have been reported.[9-13,16,17] MA derivatives have also been used as curing agents for epoxy resins.[18-21] Nevertheless, thermosetting resins employing small molecular MA derivatives as monomers have not been reported yet. On the other hand, thermal decomposition of MA groups evolves CO_2 and acetone moelcules and forms the higly reactive ketene groups.[9-13] The evolved CO_2 and acetone molecules could generate molecular-level cavities in the matrix,[22] so as to trap air inside the materials and conseuqently reduce their dielectric constants. Based on the molecular design concept, in this work a new class of MA based thermosetting resins having inherent low-*k* values of about 2.0 at 1 MHz has been demonstared (**Figure 1**). Two MA derivatives possessing furan and styrene groups are synthesized and used as the monomers for

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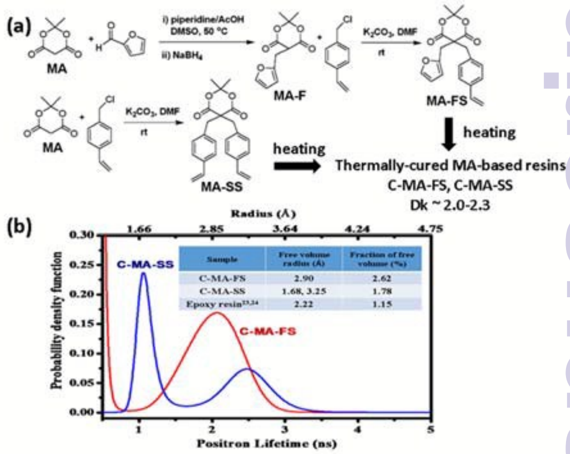
Electronic Supplementary Information (ESI) available: [Experimental method, monomer characterization and thermal properties, and thermosetting thermograms]. See DOI: 10.1039/x0xx00000x preparation of MA-based crosslinked polymers. One MA compound possesses one furan group and one styrene group (coded as MA-FS), and the other one possesses two styrene groups (coded as MA-SS). These two compounds are utilized as self-crosslinkable monomers for preparation of the corresponding thermosetting resins (C-MA-FS and C-MA-SS) with a thermal process (at 250 °C for 2 h). This is the first report on uses of MA-based small molecules as thermally-curable monomers for preparation of thermosetting resins. **Table 1** collects the basic properties of the obtained thermosetting resins. C-MA-FS and C-MA-SS exhibit a dielectric constant (Dk, at 1 MHz) of about 2.0 and 2.3, respectively. The dielectric constants of the obtained resins are relatively low compared to the values of general epoxy resins (~3.8) and polyimides (~3.6). The dissipation factor (Df) recorded with the samples are about 0.015, which is comparable to the values of general epoxy resins. The dielectric properties of C-MA-FS and C-MA-SS lead them be attractive dielectric materials for printed circuit boards, IC substrates, and encapsulants of microelectronics. In the curing reactions, formation of ketene groups accompanies with releases of CO_2 and acetone[9-13] so as to generate some cavities and pores in the cured resins.[22] As a result, air is trapped in the resins and contributes to lower the dielectric constants of the resins. To study this issue, C-MA-FS and C-MA-SS are applied to a Positron Annihilation Lifetime Spectroscopy for detecting their pore sizes and fractions of free volume. As shown in Figure 1, both samples exhibit some cavities with sizes in 2.5-3.5 Å, which are larger than the cavity sizes (2.22±0.12 Å) of free volume measured with general epoxy resins (tetraglycidylether of 4,4'-diaminodiphenylmethane or diglycidylether of bisphenol A cured with 4,4'-diaminodiphenylsulfone).[23,24] Moreover, the fractions of free volume of C-MA-FS and C-MA-SS is 2.62 % and 1.78 %, respectively. Both are still larger than the values of 1.15±0.19 % recorded with the above-mentioned epoxy resins. Both of the large cavity sizes and high fractions of free volume warrant high air contents trapped in C-MA-FS and C-MA-SS, so as to reduce their dielectric constants. On the other hand, it is noteworthy that C-MA-SS exhibits a bimodal distribution of free volume pore sizes, suggesting the resin could be of highly selective for gas permeation.[22] Together with the high free volume fraction which might contribute to high gas permeability, C-MA-SS could be a highly potential material for gas separation application. Further studies are under processing.

The thermomechanical properties of C-MA-FS and C-MA-SS are measured with a dynamical mechanical analyzer (DMA) at a heating rate of 10 °C min^{-1}. The storage modulus of C-MA-FS is about 2.72 and 0.42 GPa at 50 and 250 °C, respectively. The values recorded with C-MA-SS are 2.40 GPa at 50 °C and 1.83 GPa at 250 °C. The high mechanical strength of the resins is noteworthy. C-MA-SS might have a relatively high crosslinking density compared to C-MA-FS, due to its high storage modulus at the temperatures above the glass transition temperature (Tg). Moreover, the Tg's of C-MA-FS and C-MA-SS read from the DMA thermograms (tanδ peak) is about 214 and 252 °C, respectively. The relatively high Tg's of C-MA-FS and C-MA-SS could be attributed to their high contents of cyclic structures, which seriously restrict the chain mobility. The relatively low Tg of C-MA-FS might be understood with its high fraction of free volume and low crosslinking density, compared to C-MA-SS.



Sample	Free volume radius (Å)	Fraction of free volume (%)
C-MA-FS	2.90	2.62
C-MA-SS	1.68, 3.25	1.78
Epoxy resin[23,24]	2.22	1.15

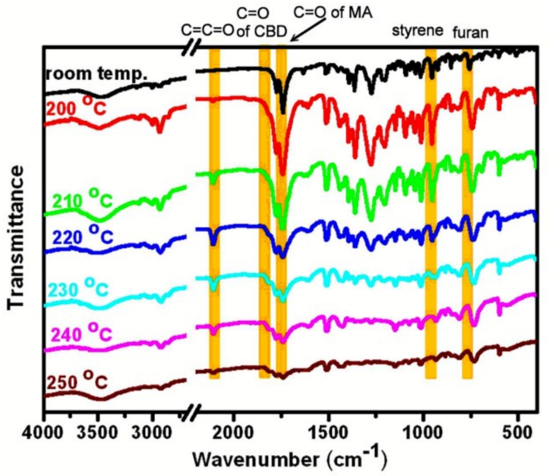
Figure 1. (a) Preparation of Meldrum's acid based monomers for preparation of low-k thermosetting resins; (b) Positron annihilation lifetime spectra of C-MA-FS and C-MA-SS resins. The free volume radius and fraction of free volume are collected in the table. The data of epoxy resins ((tetraglycidylether of 4,4'-diaminodiphenylmethane or diglycidylether of bisphenol A cured with 4,4'-diaminodiphenylsulfone) from literature[23,24] is added for a comparison.

Nevertheless, the Tg's of the MA-based resins are higher than the values of conventional bisphenol-A based epoxy and benzoxazine[25,26] resins (about 140-190 °C). The thermal stability, which is recorded at the 5 wt% weight loss (T_{d5}) in thermogravimetric analysis (TGA) in nitrogen, is 365 and 362 °C for C-MA-FS and C-MA-SS, respectively. The thermal stability is high enough to meet the general requirements for applications in microelectronics and optics. Both resins show rapid weight losses at about 420 °C in nitrogen. The weight fraction of the sample residual at 800 °C in TGA analysis is taken the char yield of the sample. C-MA-FS and C-MA-SS give a high char yield of 39 wt% and 21 wt%, respectively. The resins exhibit similar thermal stability in air. Nevertheless, oxidation reaction of the resin residuals occurs at high temperatures so as to result in a second-stage of weight loss at about 500-600 °C.

Table 1. Properties of MA-based thermosetting resins.

Sample	T_g (°C)		Storage modulus (GPa)		T_{d5} (°C)	Char yield (wt%)	Dk at 1 MHz	Df at 1 MHz
	DSC	DMA (tanδ)	50 °C	250 °C				
C-MA-FS	202	214	2.72	0.42	365	39	2.0	0.015
C-MA-SS	222	252	2.40	1..83	362	21	2.3	0.0[illegible]5

Decomposition of the MA groups of MA-FS and MA-SS would generate the highly reactive ketene groups with releases of CO_2 and acetone.[9-13] Two major reactions, including dimerization and nucleophilic addition, have been reported to the ketene groups.[9] As MA-FS and MA-SS do not possess a nucleophile group, dimerization of ketene groups could be the major reaction for the two compounds in the thermally curing process. Nevertheless, as the monomers only have one MA unit, dimerization of the generated ketene groups would not result in crosslinked structures. Other intermolecular reactions should take place in the curing process. Hence, the reactions of MA-FS under a heating process have been traced with a Fourier transform infrared spectroscopy (FTIR, **Figure 2**). The FTIR spectrum of MA-FS recorded at room temperature shows the C=O absorption of MA groups at 1740 and 1774 cm^{-1}. The absorption of ketene groups at about 2103 cm^{-1} appeared in the FTIR spectrum recorded at 200 ^{o}C, indicating the performance of thermolysis reaction of the MA group and generation of the ketene groups. The reaction temperature is coincident to those obtained in the thermal analysis (DSC and TGA). Meanwhile, The absorption peak at about 1815 cm^{-1}, which somewhat overlaps with the C=O absorption of the MA group, corresponds to the absorption of cyclobutane-1,3-dione (CBD) groups which are formed with the dimerization reaction of the ketene groups.[9] The result supports to that in the heating process the MA-FS generates ketene groups with the thermolysis reaction of MA groups and consequently performs the dimerization reaction of ketene groups to result in intermolecular linkages with the CBD groups. The peak intensity of the ketene group increases first, and then decreases with further increasing the temperatures to 230-250 ^{o}C. The absorption intensity of the CBD group increases with the increases in temperatures. As a result, the extents of both the thermolysis of MA groups and dimerization of ketene groups increases with increasing temperatures. Moreover, the absorptions of the styrene moiety at 1631 (C=C) and 954 cm^{-1} (C-H) decrease in the spectra recorded at high temperatures, suggesting the C=C group of the styrene moiety might possibly involve in the MA thermally-curing reactions. Nevertheless, the dramatic decrease in the absorbance of the styrene moiety at 220-230 ^{o}C could be attributed to the self-polymerization of the styrene groups. A similar result is also observed with the specific absorption of the furan group at about 756 cm^{-1}, which shows a decrease in the peak intensity at temperatures above 220 ^{o}C. However, the quantitative analysis on the furan groups might be interfered with other groups formed in the crosslinking process, such as the C=C groups formed with the Diels-Alder (DA) reaction between ketene and furan groups. Moreover, the thermal decomposition of MA groups and the sequential reaction of the formed ketene groups have been traced with a ^{1}H NMR using MA-F as a model compound (see supporting materials). MA-F was reacted at 160 ^{o}C for 10 min and the reaction residual was applied to ^{1}H NMR measurement.[9] The acetone molecules generated with the MA group decomposition are trapped in the reaction product to exhibit the resonance peak at 2.10 ppm. The occurrence of the Diels-Alder reaction between ketene and furan groups is demonstrated with the resonance peaks at about δ = 5.80-6.20 ppm corresponding to the -C***H***=C***H***- groups of the DA adduct. Although the above results suggest that both the styrene and furan groups could be possibly involved in the crosslinking reactions with the ketene groups, more detail studies are needed in the future work.



Normalized FTIR absorbance of functional groups in MA-FS thermally-crosslinking process

Temperature (^{o}C)	Ketene	CBD	Furan	CH=CH$_2$ of Styrene
25	0.00	0.00	2.13	2.00
200	0.15	0.00	2.13	2.00
210	0.40	0.00	1.96	1.77
220	1.05	0.05	1.69	1.12
230	0.92	0.12	1.67	0.01
240	0.60	0.13	1.63	< 0.01
250	0.34	0.14	2.18	< 0.01

Figure 2. FTIR spectra of MA-FS recorded at different temperatures to trace the reactions taking place in the thermally-curing process. The sample was kept at each temperature for 10 ^{o}C in the process. The data collected in the table presents the absorbance of the functional group normalized normalized with the absorabnce of the unchanged phneyl group.

Based on the above results, the reactions involve in the thermally-curing reaction of MA-FS could be tentatively proposed to be (**Figure 3)** (i) the dimerization reaction of ketene groups, (ii) the [2+2] addition reaction between the ketene and styrene groups, (iii) the [2+4] DA reaction between the ketene and furan groups, and (iv) the self-polymerization of styrene groups. As MA-SS does not possess a furan group, reaction (iii) is not involved take place in the thermally curing reactions of MA-SS. As a result, MA-FS and MA-SS might be possibly considered as trifunctional ABB' and AB$_2$ monomers (A: MA group; B: styrene group; B': furan group) respectively. The A group is reactive toward both B and B' groups. Moreover, the A group is highly reactive toward self-dimerization which provides additional reaction to link the monomers. As a result, MA-FS and MA-SS are not like conventional AB$_2$ monomers which result in hyperbranched product in polymerization, and tend to form 3-dimensional networks.

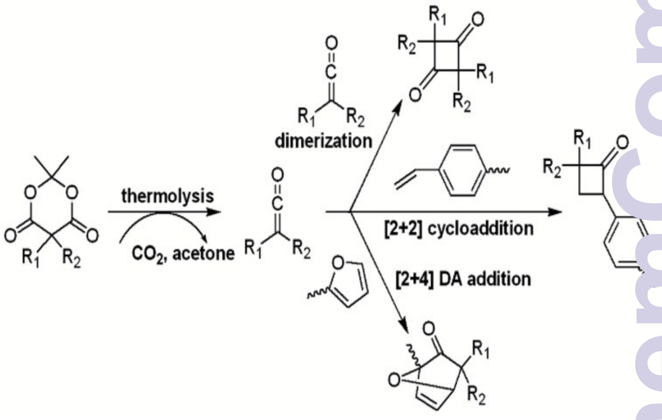


Figure 3. Reactions in the thermally-crosslinking process of MA-FS.

MA-FS and MA-SS show a melting point of about 117 and 177 ^{o}C, respectively. At high temperatures, both compounds exhibit exothermic peaks in the DSC thermograms. The exothermic behavior of MA-FS starts at about 180 ^{o}C and shows a maximum peak at about 223 ^{o}C, which is coincident to the weight loss behavior of MA-FS in TGA. The exothermic and weight loss behavior of MA-FS is attributed to the thermal decomposition of the MA group, which would release one CO_2 and one acetone molecules and result in a weight loss of 30 wt%. The weight loss of MA-FS recorded with TGA (about 32 wt%) is agree with the theoretical value. MA-SS show similar results in thermal analysis, in which it exhibits an exothermic peak at about 195 ^{o}C in DSC measurement. It can be seen that MA-FS possesses a wide processing window (the temperature difference between melting point and reaction temperature) of about 70 ^{o}C. The processing property of MA-SS for molten processes is relatively poor. Nevertheless, both MA derivatives are soluble in common organic solvents and could be processed with conventional solution processes.

In conclusion, MA derivatives have been demonstrated as suitable thermally-curable monomers for preparation of thermosetting resins through the ketene-based chemistry. A new class of thermosetting resins has been explored to show low dielectric constants, high glass transition temperatures, good thermal stability, and high mechanical strength. Moreover, the in situ formation of cavities in the cured resins result in relatively large free volume pore sizes and high free volume fractions, making the obtained MA-based resins are potentially applicable for gas separation.

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