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The evolution of nanopores in allylated calixarene resin during thermal cure

Zhuo Wang^{a,b}, Huan Wang^{a,b}, Penggang Ren^a, and Mingcun Wang^b

^aFaculty of Printing and New Electronic Media, Xi'an University of Technology, Xi'an, China; ^bSchool of Chemistry, Beihang University, Beijing, China

ABSTRACT

In this paper one kind of new thermosetting resin, allyl etherified calixarene (allylated calixarene), was prepared and investigated. Claisen rearrangement reaction could not occurred due to the existence of para-positioned substituent in allylated calixarenes, and thermal cure proceeded at comparably low curing temperature (210–230 °C, lower than the curing temperature of allylated Bisphenol-A and allylated phenol-formaldehyde prepolymer at 330 °C). Allylated p-methylcalixarene cannot remain its nanopore conformation (i.e., cone conformation) even before its thermal cure. Allylated p-tert-butylcalixarene can keep its cone conformation at room temperature and low curing temperature (e.g., <130 °C), however its nanopores will be destroyed upon heating at high temperature (the gradually level-off and quietly weak diffraction peak in the Small Angle X-ray Diffraction profile). Allylated p-phenylcalixarene can preserve its nanopore conformation at room temperature and high curing temperature (e.g., 200 °C). The results indicated that the larger para-substituent will hinder the inversion of phenolic ring, and the higher curing temperature will promote the rotation of phenolic ring.

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1. Introduction

Calixarene is one kind of annular phenol-formaldehyde condensate, in which the ring is composed with phenol units connected via methylene bridges at ortho sites of phenol units;^[1] many calixarene derivatives have been developed through chemical functionalization of hydroxyl and alkyl groups at phenolic rings' lower and upper rims.^{[2],[3]} One-step-method is the widely accepted preparation protocol up to now,^[4] p-tert-butylcalix[n]arenes (n = 4, 6, and 8, etc.) are readily synthesized when p-tert-butylphenol and formaldehyde are heated in appropriate solvent under catalysis of alkaline. Owing to the small hydroxyl groups, several conformations (cone, partial cone, 1,2-alternating and 1,3-alternating conformations, etc.) can be formed through the inversion of phenolic ring, as shown in Figure 1.^[5]

The conformation of calixarene can be well solidified by replacement of hydroxyl with big groups such as butyl and benzyl groups. Gutsche CD et al chemically modified p-tert-butylcalix[4]arene and p-allyl-calix[4]arene into etherified species by methyl, ethyl, allyl, benzyl and trimethylsilyl; the cone conformation cannot be maintained when etherified by methyl and ethyl groups, while etherified by benzyl and trimethylsilyl groups the cone conformation can be maintained.^[6] The technique of ¹HNMR was applied to find that the etherified or esterified calix[6]arene and calixa[8]arene are more flexible than the corresponding calix[4]arene, however etherification of calix[6]arene by trimethylsilyl still

guaranteed the preservation of cone conformation.^[7] As for calixarenes modified by methoxycarbonyl, the derivative had the cone, partial cone and 1,3-alternating conformations; and such calixarene derivatives were used to recover harmful ions proficiently from nuclear fuel waste.^[8]

Crosslinkable groups (such as alkynyl, allyl, epoxy and nitrile) can be chemically grafted onto calixarene, and it is regarded as an effective pathway to generate new thermosetting calixarene-based resins for the application of polymer matrix of advanced high temperature composite materials, however such resins have been scarcely reported yet.^[9] The convenient way for calixarene thermosetting resins preparation is etherification and esterification of phenolic hydroxyls. Novel calixarene derived thermosetting resins will attract high interests, if considering the combined properties of resin (material processability, mechanical performance) and calixarene (nanoporous structure, light weight, oxidation resistance). Unfortunately, up to now the applications of calixarene in thermosetting resins has been focused mainly on curing agent of phenolic or epoxy resins,^{[10],[11]} calixarene-derived vinyl ester resin^[12] and epichlorohydrin-containing photo-polymerizable resin.^[13] In a recent report by the author of M Wang,^[14] p-tert-butylcalix[4]arene cyanate ester resin was prepared, and its thermal cure behaviors and high thermal stability were evaluated.

In this paper, allylated calixarenes were successfully prepared, and the trend of nanopore evolution upon thermally cross-linking heat-treatment was investigated. The effects of

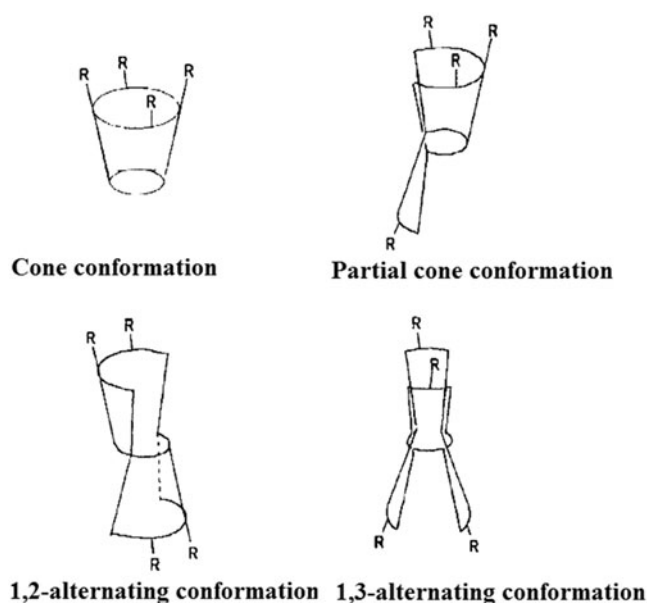


Figure 1. Four conformations of p-tert-butylcalix[4]arene.

various thermally curing temperatures and different-sized para substituents on nanopore revolution were studied respectively. Based on the results, proper calixarene allyl derivative and suitable curing agents can be screened to get thermally curable calixarene with preserved nanopore conformation.

2. Experimental

2.1. Materials

The starting reagents of p-tert-butylphenol p-methylphenol and p-phenylphenol were obtained from Sigma-Aldrich, and were used as received ACS grade. Paraformaldehyde and allyl bromide (Analytical Reagent) were from Beijing Chemical Works.

2.2. Synthesis of calixarenes

Calixarenes were prepared according to the procedure as described in literature.^[15] In a typical synthesis of p-tert-butylcalix[4]arene, p-tert-butylphenol (90 g, 0.6 mol), NaOH (1.8 g, 0.045 mol) and 5 mL de-ionized water were added inside a 3-neck flask, and a red solution was formed after stirring at 100 °C. Paraformaldehyde (18 g, 0.6 mol) was added in batches in an interval of 1 h, and the reaction was refluxed at 100 °C for 2 h to become yellow solid.

The above solid (15 g) was placed in another 3-neck flask, 100 mL diphenyl ether was added, the heat-treatment was conducted for 3 h at 200 °C. After cooling down, 200 mL methanol was added as precipitant. After vacuum filtration, a grayish powder was obtained; the precipitate was rinsed with de-ionized water until it became white. Pure calixarene was recovered upon dry in convection oven at 120 °C overnight.

P-methylcalixarene and p-phenylcalixarene were prepared according to the same procedure.

2.3. Synthesis of allyl etherified calixarenes

Following a similar synthetic protocol of allyl etherified bisphenol-A and allyl etherified phenol-formaldehyde resin,^[16] p-tert-butylcalix[4]arene and allylbromide were mixed at a molar ratio of 1:1.2 in butanone, sodium hydroxide (10 wt% aq) was introduced as de-acid reagent, and the reaction was controlled at around 70 °C until the pH value reached about 7. Yellowish powder of allylated p-tert-butyl calix[4]arene was recovered after filtration, washing with deionized water and drying. Other allyl ethers of calixarenes were synthesized with a similar process.

2.4. Thermal cure of different allyl etherified calixarenes

Allylated p-tert-butylcalix[4]arene was thermally cured for 3 h at 200 °C. P-methylcalixarene and p-phenylcalixarene allyl ethers were cured under the same conditions. Allylated p-tert-butylcalix[4]arene with 20% hydrosilicone oil as cross-linking agent was thermally cured at 130 °C for 6 h and 80 °C for 10 h respectively under the catalysis of 0.1% Pt.

The degree of thermal cure was determined qualitatively by tetrahydrofuran distillation at boiling state for 4 h, and was represented by the proportion of non-extractive in the cured material.

2.5. Characterizations

Fourier infrared spectrum (FT-IR) was recorded on Nicolet iS50 (wave number range of 3800–800 cm⁻¹, resolution of 4 cm⁻¹, scanning times 32, KBr tablet). Differential Scanning Calorimetric profile (DSC) was recorded on Mettler-Toledo DSC1Q2000 (nitrogen flow at 50 mL/min, temperature range of 40–350 °C, and heating rate at 10 °C/min). ¹H NMR was recorded on Bruker 400 using CDCl₃ as the solvent. The elemental analysis was performed on Euro Vector EA3000 (oxygen content was obtained by difference). Small Angle X-ray Diffraction was measured on Shimadzu XRD-7000s (scanning range of 0.6–10°, scanning rate of 0.3°/min). Thermogravimetric analysis (TGA) were performed on a TA Instrument DSC3+ in the temperature range of RT–800 °C under nitrogen atmosphere (10 mL/min) with a 10 °C/min heating rate. Dynamic mechanical analysis (DMA) were tested on NETZSCH DMA 242E at 1 Hz at a temperature ramp of 3 °C/min ranging from 50 to 400 °C under a N₂ flow at 50 mL/min.

3. Results and discussion

3.1. Synthesis of various allyl etherified calixarenes

As shown in Figure 2, allyl etherified calixarene was synthesized in three steps: the condensate of phenol and formaldehyde under basic catalysis; cyclization of the condensate at higher temperatures to form calixarene; etherification of calixarene by allylbromide under basic catalysis.

Before etherification, at room temperature the stable conformation of p-tert-butylcalix[4]arene is cone conformation (owing to the strong hydrogen bonds of phenolic hydroxyl

groups). While the hydroxyls were substituted by big volume groups via etherification and esterification, hydrogen bonds will be destroyed, then some other conformations (such as semi-cone, 1,2-alternating and 1,3-alternating conformations) will exist stably because of the free rotation of phenolic rings, the conformations change resulted in the revolution of nanopores in calixarenes. The increase of

temperature in thermal cure of allylated calixarene plays the similar influence.

In order to preserve the nanopore structure or conformation at higher temperature during thermal cure of allylated calixarene, the following two methods were used in this research: (1) the low-temperature thermal-cure can be readily realized for allyl etherified calixarene, thus the nanoporous cone conformation cannot be destroyed at low temperature; (2) big substituent on para sites of phenolic rings in allylated calixarene can hinder the rotation of phenolic rings, thus can preserve cone conformation and nanoporous structure.

The molecular structure was characterized by the methods of Elemental analysis and FT-IR, and the results were shown in Table 1 and Figure 3. Based on EA data in Table 1, compared the calculated oxygen content with the measured oxygen content, it can be concluded that there was still minor amount of unsubstituted hydroxyl in allylcalixarenes (oxygen content, found value > calculated value). Similar information was implied in Figure 3, the peaks of allyl and benzene rings can be found clearly at 1640, 1600 and 1500 cm^{-1} ; aromatic and aliphatic C-H bonds exhibited characteristic peaks at 3050 and 2930 cm^{-1} respectively; the weak peak at 3400 cm^{-1} probably indicated the minor amount of remaining hydroxyl in allylcalixarenes. The existence of allyl ($-\text{CH}_2-\text{CH}=\text{CH}_2$ at 5.6–6.2ppm, $-\text{CH}_2-\text{CH}=\text{CH}_2$ at 4.2–4.5ppm), benzene rings (ph-H at 6.9–7.4) and bridged methylene ($-\text{CH}_2-$ at 3.6–3.9) was revealed by ^1H NMR test.

Prior to etherification by allyl groups, each calixarene with different para substituent exhibited strong peak attributing to melting point (minor impurity in p-tert-butylcalixarene and p-methylcalixarene); as indicated by Figure 4, after etherification to allylcalixarene, the melting point of calixarene disappeared and a well-defined exothermic peak emerged at 210, 225 and 230 $^{\circ}\text{C}$ for allyl(p-phenyl)calixarene, allyl(p-methyl)calixarene and allyl(p-tert-butyl)calixarene respectively. In

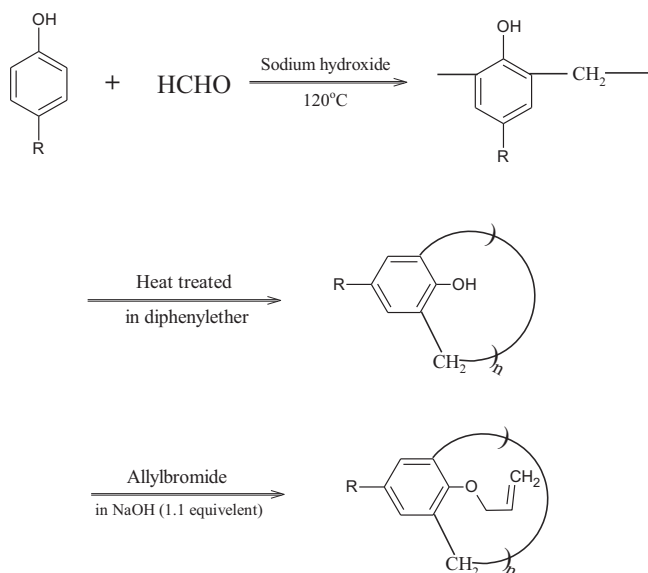


Figure 2. Synthetical route of allyl-etherified calixarenes.

Table 1. Elemental analysis results of varying allylcalixarenes.

| Element | content (% by weight) | Allyl(p-tert-butyl) calixarene (%) | Allyl(p-methyl) calixarene (%) | Allyl(p-phenyl) calixarene (%) |
|---------|-----------------------|------------------------------------|--------------------------------|--------------------------------|
| H | Calculated | 8.9 | 7.5 | 6.3 |
| | Found | 9.0 | 7.6 | 6.2 |
| C | Calculated | 83.2 | 82.5 | 86.5 |
| | Found | 82.5 | 81.6 | 85.7 |
| O | Calculated | 7.9 | 10.0 | 7.2 |
| | Found | 8.5 | 10.8 | 8.1 |

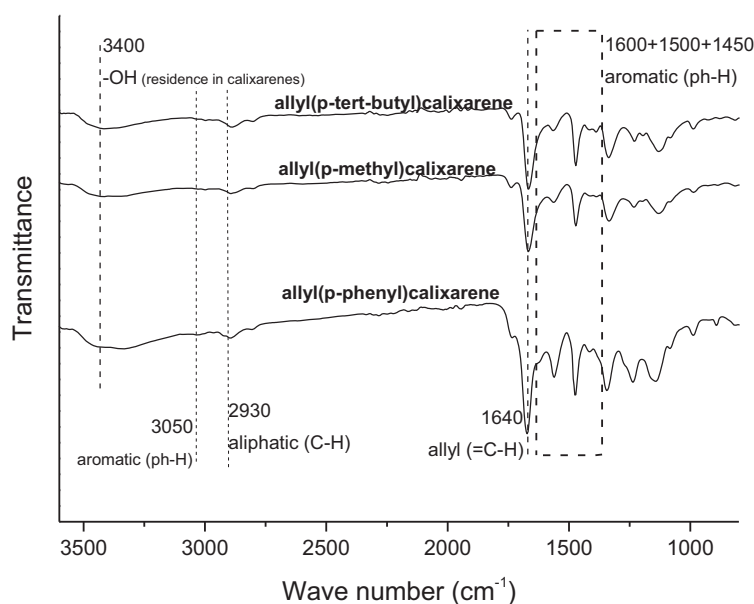


Figure 3. FT-IR spectra of allylcalixarenes.

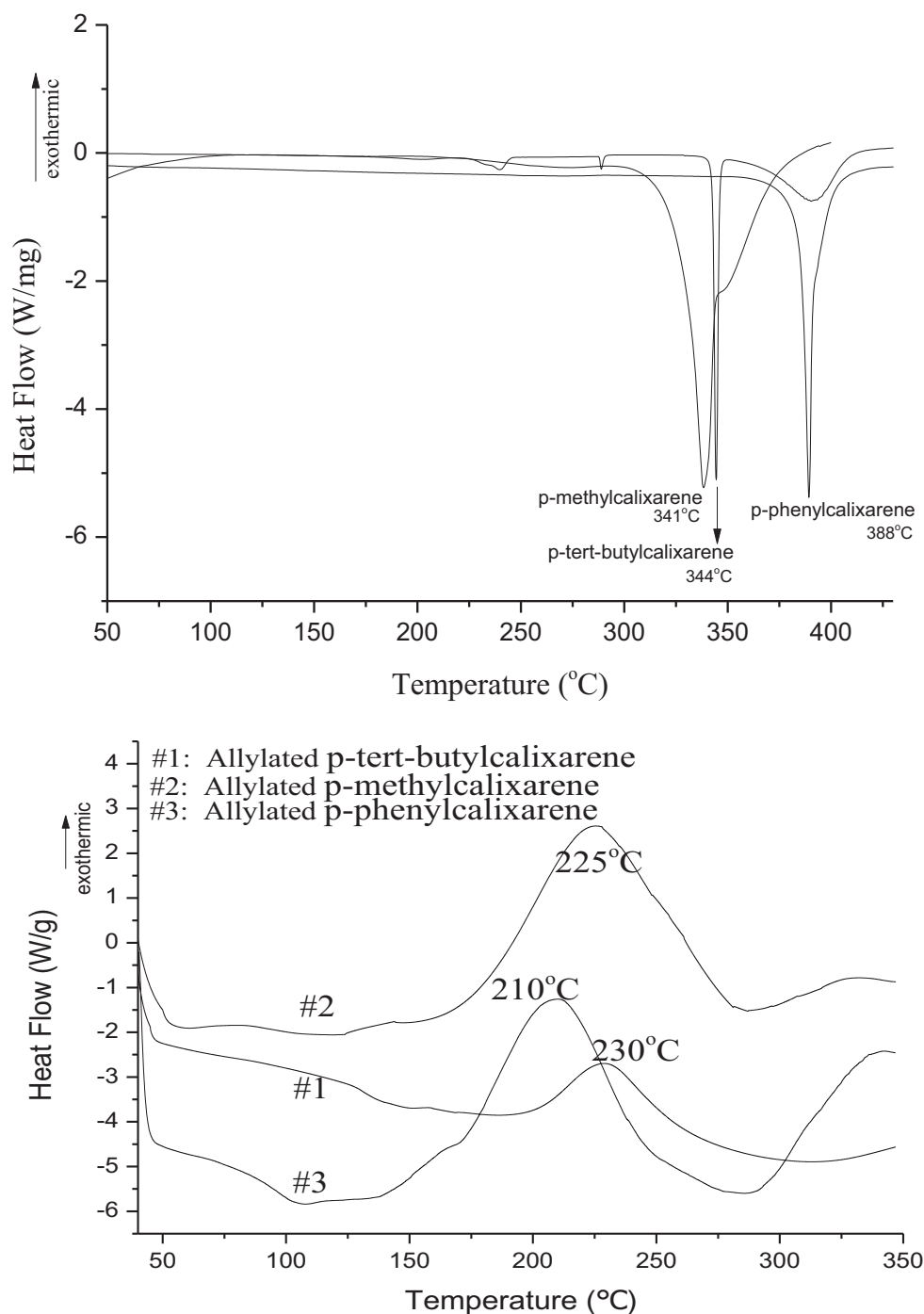


Figure 4. DSC profile of calixarenes and their allylcalixarenes.

Figure 4, the results showed that the cure peak temperature was around 210–230 °C: for allylated p-tert-butylcalixarene, the exothermic peak was in the range of 200–260 °C and peaking at 230 °C; for allylated p-methylcalixarene, the exothermic peak was in the range of 180–280 °C and peaking at 225 °C; for allylated p-phenylcalixarene, the exothermic peak was in the range of 170–270 °C and peaking at 210 °C. The para-substituent seems to have little effect on the exothermic profile, but have an unavoidable influence on the peak position. At higher than 300 °C, the profile started to climb up, which probably resulted from the initiation of thermal decomposition (as shown in Figure 5, mass loss started slowly beyond such high temperatures).

It was well known that Claisen rearrangement will occur at about 250 °C for allylated phenolic ether compounds such as allyl etherified bisphenol-A and allyl etherified phenol-formaldehyde prepolymer, and the polymerization of allyl groups will proceed at about 330 °C;^{[17],[18]} so N,N-4,4-diphenylmethyene bismaleimide was always used to chemically modify allylated phenolic substances via Diels-ene addition reaction to prepare useful high-performance resins.^[19] However, for allylated calixarenes in this paper, the thermal behavior is quite different because Claisen rearrangement cannot take place due to the full substitution of ortho and para sites of phenolic rings. As shown in Figure 3, allylated calixarenes (including allyl p-tert-butylcalixarene, p-methylcalixarene

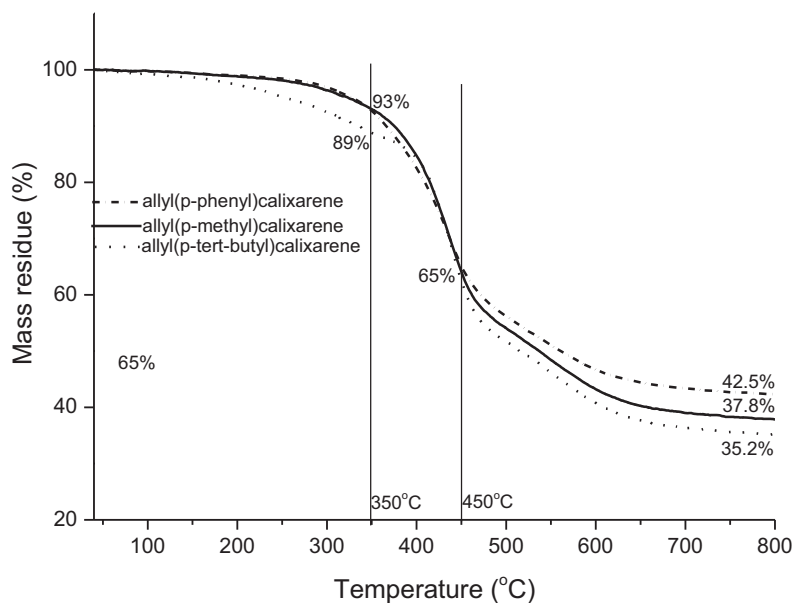


Figure 5. TGA profile of allylcalixarenes in nitrogen atmosphere (thermally cured under 0.1%Pt catalysis at 80 °C 10h).

Table 2. Thermal curing degree of different allylcalixarenes.^a

| Thermally cured resin | Curing conditions | | |
|-------------------------------|-------------------|---|---|
| | 200 °C 3h (%) | 20% hydrosilicone oil and 0.1%Pt, 130 °C 3h (%) | 20% hydrosilicone oil and 0.1%Pt, 80 °C 10h (%) |
| Allyl(p-tert-butyl)calixarene | 99.5 | 98.8 | 97.9 |
| Allyl(p-methyl)calixarene | 99.4 | 98.7 | 98.0 |
| Allyl(p-phenyl)calixarene | 99. % | 99.1 | 98.5 |

^aNote: degree of thermal cure is (1-extractive percentage) × 100%.

and p-phenylcalixarene) exhibited only one exothermic peak at 210–230 °C, corresponding to allyl ether's polymerization.

The degree of thermal cure of different allylcalixarenes were qualitatively determined by tetrahydrofuran distillation and listed in Table 2, the results showed: (1) with the increase of thermal curing temperature, thermal cure degree was slightly increased, and in all cases thermal curing degree reached $\geq 98\%$. (2) assisted by curing agent and metallic catalyst, thermal cure could proceed at quite mild conditions such as 80 °C 10 h or 130 °C 3h.

Thermal stability of the cured allylcalixarenes was significantly expected, and the results of TGA profiles of allylcalixarenes thermally cured under 0.1% Pt catalysis at 80 °C 10 h were exhibited in Figure 5 (in view of the existence of nano-pores at lower curing temperatures, so thermal cure at low temperatures was preferred). Ascertained by the results in Figure 5, allylcalixarenes possessed good thermal-decomposition resistance: (1) the carbon residue at 800 °C gradually increased in the sequence of allyl(p-tert-butyl)calixarene, allyl(p-methyl)calixarene and allyl(p-phenyl)calixarene. (2) the maximum decomposition rate was at about 450 °C where a mass residue of 65% was found. (3) thermal decomposition was initiated at around 300–350 °C, implying allylcalixarenes are among the family of high temperature resins.

Another technique to evaluate thermal stability of the cured allylcalixarenes was DMA, and the results of DMA profiles of allylcalixarenes thermally cured under 0.1% Pt catalysis at 80 °C 10 h were exhibited in Figure 6 (T_g was

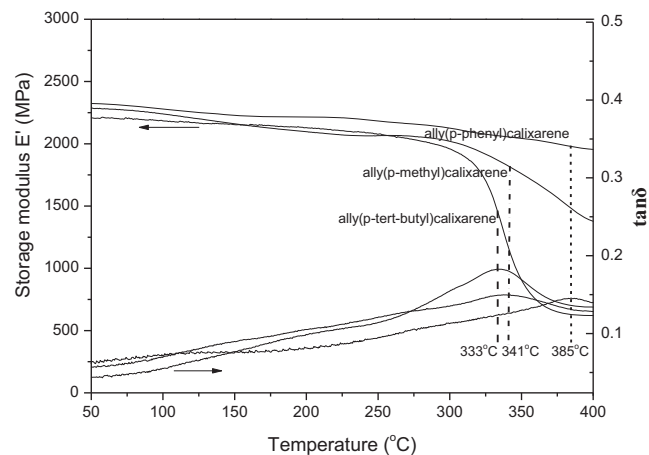


Figure 6. DMA profile of allylcalixarenes in nitrogen atmosphere (thermally cured under 0.1%Pt catalysis at 80 °C 10h).

expressed by the peaking temperature of $\tan\delta$ profile). Although thermal cure was processed at such a low temperature, the cured allylcalixarene materials exhibited interesting high-temperature resistance: (1) in the sequence of allyl(p-tert-butyl)calixarene, allyl(p-methyl)calixarene and allyl(p-phenyl)calixarene, glass transition temperature gradually climbed higher from 333 °C to 385 °C, revealing the important effect of para substituent on T_g . (2) even allyl(p-tert-butyl)calixarene possessed high thermomechanical resistance, which indicated the possibility of application of allylcalixarene for high temperature low-weight polymeric material.

Figure 7 showed the small angle XRD profiles of three calixarenes: for p-tert-butylcalixarene, because of the big para-substituent of tert-butyl group, the diffraction peak was sharply strong and narrow, indicating the pure composition of p-tert-butylcalixarene; for p-phenylcalixarene, the diffraction contained several peaks and showed a strong and narrow profile, indicating the effective hinderance of phenolic ring rotation and almost fixed conformations; for p-

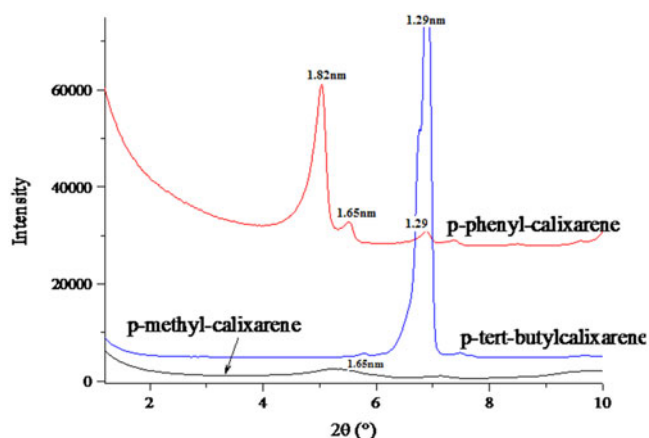


Figure 7. SAX spectra of p-tert-butylcalixarene, p-phenylcalixarene and p-methylcalixarene.

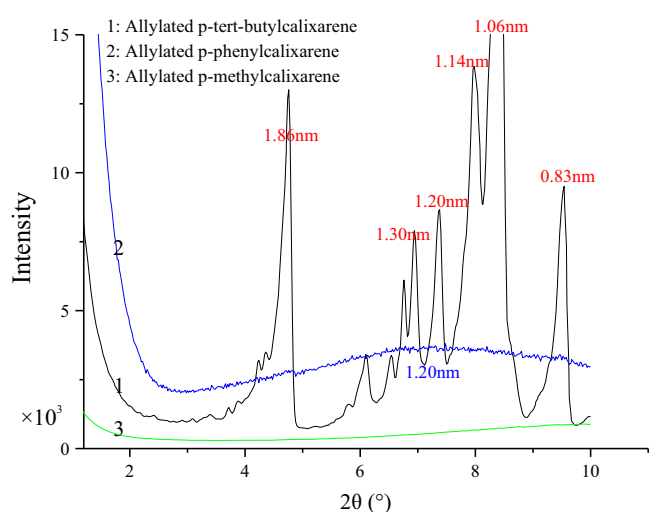


Figure 8. SAX spectra of allylated calixarenes.

methylcalixarene, the diffraction peak was weak and wide, indicating the complex conformations due to rapid transformation of calixarene conformations. So, if a nanoporous calixarene allyl ether resin is required in practical applications, p-tert-butylcalixarene and p-phenylcalixarene are the most suitable parent raw-materials, while p-methylcalixarene is not proper as the starting material.

The SAX profiles of allylated calixarenes were shown in Figure 8: (1) for allylated p-tert-butylcalixarene, there are several diffraction peaks, corresponding to different substitution degree of allyl derivatives, but the nanopores were preserved well. (2) for allylated p-phenylcalixarene, there is a quite broad peak, implying the cone conformation was not retained definitely, but still was the major state. (3) for allylated p-methylcalixarene, there is no apparent peak in the SAX profile, implying the complex conformations and no regular nanopores after etherification by allyl.

3.2. Nanopore evolution during various thermally curing temperatures for allylated p-tert-butylcalix[4]arene

Compared calixarenes with big and small substituents at phenolic ring's para sites, the XRD diffraction intensity of p-

tert-butylcalixarene was much higher than that of p-methylcalixarene. While hydrogen in hydroxyls was replaced by allyl through etherification, although hydrogen bonds disappeared (meaning that the ring rotation became free), thanks to the high steric effect of allyl groups, allyl etherified p-tert-butylcalixarene can still retain its nanopore structure.^[6] Revealed by Figure 8, owing to the various etherification degrees (it is possible for etherification degrees of 1, 2, 3 and 4, respectively), a variety of nanopores with different sizes will exist in p-tert-butylcalixarene. For p-phenylcalixarene, the hinderance effect of phenyl at phenolic ring's para site is slightly lower, so the allylated p-phenylcalixarene showed a quite broad diffraction peak in the profile of SAX. For p-methylcalixarene, the disappearance of hydrogen-bonds' hinderance (hydroxyl groups) and the quite weak para-substituents' steric effect (p-methyl groups) resulted into a SAX profile without nanopores' diffraction peaks.

Allylated p-tert-butylcalix[4]arene was thermally cured under different temperatures (80, 130, and 200 °C) with certain catalyst (using 20% hydrosilicone oil as curing agent and using 0.1% Pt as catalyst), the corresponding SAX profiles were listed in Figure 9. The results showed: (1) when allylated p-tert-butylcalixarene was thermally cured at 80 °C (using 20% hydrosilicone oil as curing agent and using 0.1% Pt as catalyst), the cured allylated p-tert-butylcalixarene retained its nanopores' structures closely similar with the original uncured sample (nanopores with diameter at 1.86, 1.19, 1.14, 1.06 and 0.93 nm respectively), implying thermal cure at 80 °C did not affect the nanopore structure and the conformations were frozen in the cured resin. (2) when allylated p-tert-butylcalixarene was thermally cured at 130 °C (using 20% hydrosilicone oil as curing agent and using 0.1% Pt as catalyst), the cured allylated p-tert-butylcalixarene exhibited two diffraction peaks (corresponding to nano-diameter at 2.26 and 1.19 nm respectively), indicating the majority of conformations were transformed into more stable ones. (3) while thermally cured at 200 °C (pure resin's thermal cure without any catalysis), there was only one quietly wide and weak peak in SAX profile, implying not defined conformations in the high-temperature thermally cured resin. The above information revealed that: for p-tert-butylcalixarene with big substituent at para site of phenolic ring, in order to retain the nanoporous conformations, allylated calixarene should be thermally cured at not too high temperatures such as <130 °C.

3.3. Nanopore evolution during thermal cure of allylated calixarenes with different Para-substituent of phenolic ring

The steric effect of para-substituent in allylated calixarene has credible influence on nanopore conformation states, and cone conformation and semi-cone conformation can be preserved when big para-substituent such as benzyl group is positioned at para site of phenolic rings.^[20] In this paper, the nanopore information was investigated for allylated calixarenes with different para-substituents.

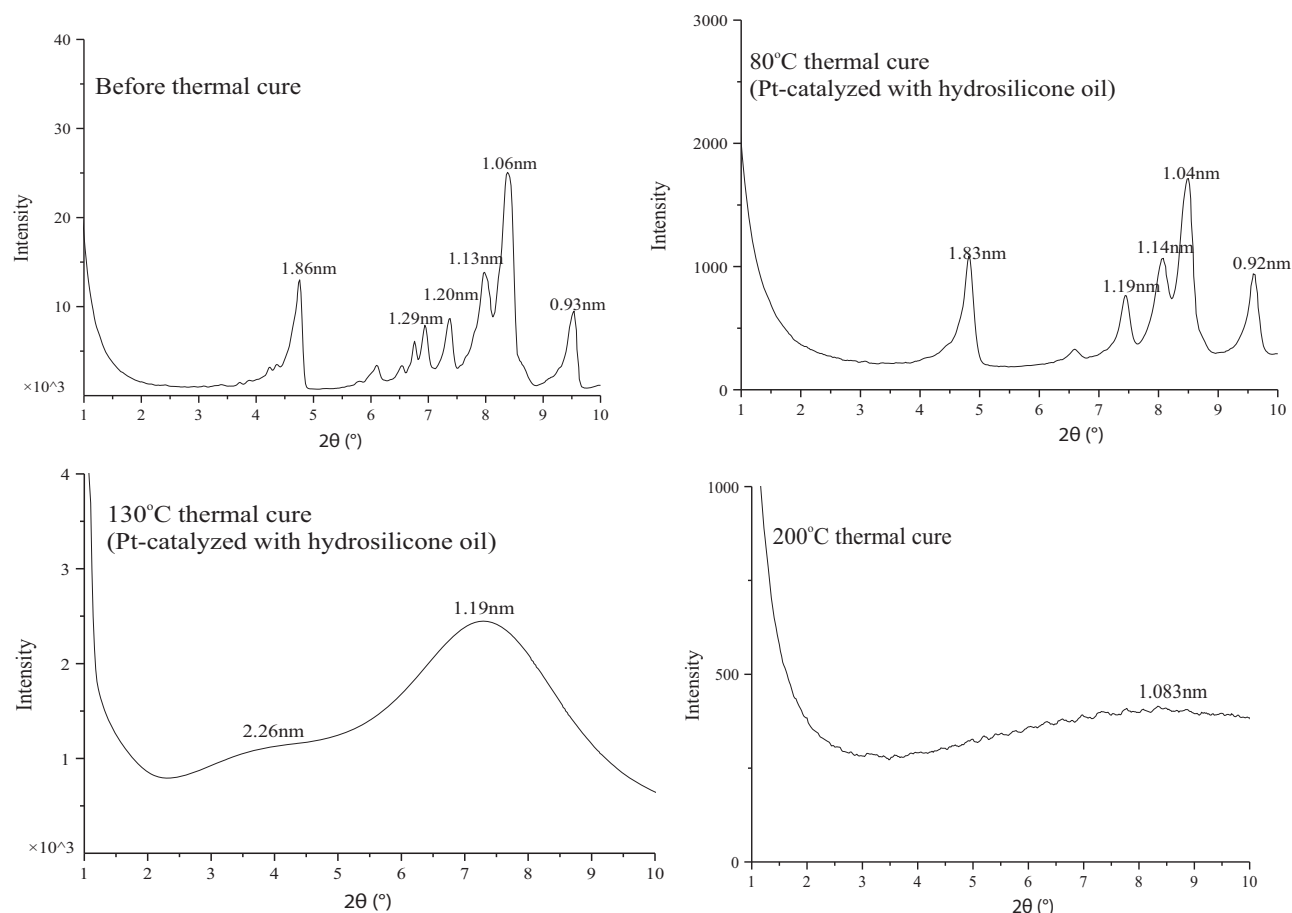


Figure 9. SAX spectra of allylated p-tert-butylcalixarenes at varying curing temperature.

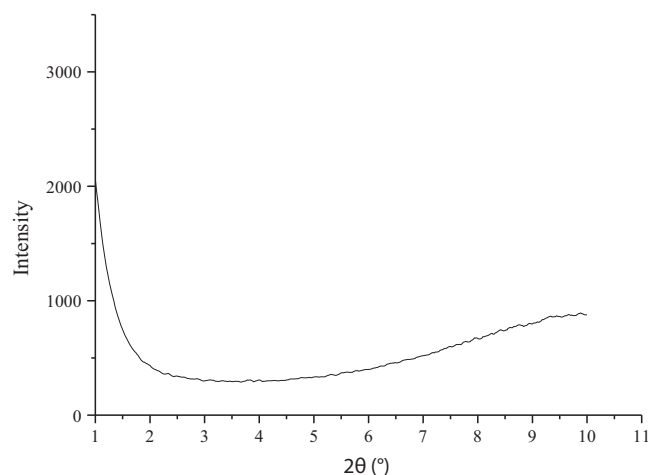


Figure 10. SAX spectra of allylated p-methylcalixarene.

As shown in Figure 10, for allylated p-methylcalixarene, the diffraction peaks in SAX profile were not detected even at uncured condition, meaning the nanopore structure cannot exist stably in the case of small para-substituent like methyl.

In the case of tert-butyl as the para substituent, allylated calixarene showed different nanopore behaviors: for the uncured sample (not thermally treated), as shown in Figure 11, the SAX profile of allylated p-tert-butylcalixarene exhibited a similar trend with that of its parent p-tert-butylcalixarene; after thermal cure at 200 °C, the SAX profile of

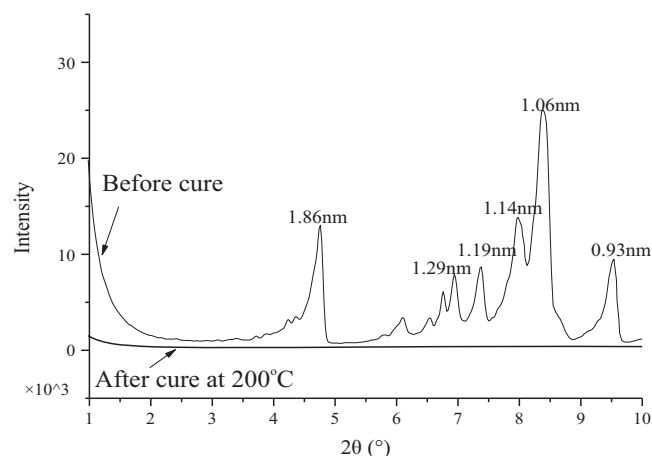


Figure 11. SAX spectra of allylated p-tert-butylcalixarene and its thermally cured sample at 200 °C.

crosslinked allylated p-tert-butylcalixarene leveled off without the trace of diffraction peaks, indicating the ruin of regular nanopore conformations during high temperature treatment at 200 °C. The above results revealed that at high temperature the ring rotation of allylated p-tert-butylcalixarene could occur; so, the comparable low temperature in thermal cure is desirable for the preservation of nanopores in crosslinked sample.

While phenyl group is the para-substituent, as revealed by Figure 12, the similar profiles were responsible for the uncured and cured samples, however the peaking position

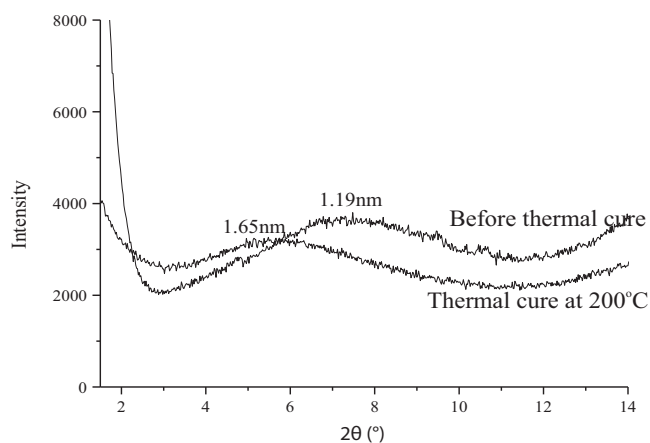


Figure 12. SAX spectra of allylated p-phenylcalixarene and its thermally cured sample at 200 °C.

shifted lower (i.e., nanopore size grew a bit). It indicated that the nanopore could be retained if a big para-substituent is positioned at the para site of calixarene's phenolic ring.

In summary, for allylated calixarene thermosetting resin, in order to have a nanoporous structure in the thermally cured material, a comparably low temperature was appreciated in thermal cure process, otherwise a para-substituent of phenolic ring should be huge enough to have sufficient steric effect for preservation of regular nanopores.

As for the possible applications of such kind of thermosetting resins with well-defined nanopores, as shown by the results of TGA and DMA analyses of thermally cured allylcalixarenes, allylcalixarenes will be ideal candidates for electromagnetic wave transparent materials in applications at high temperatures.

4. Conclusions

Based on the above results, the following conclusions can be made:

1. Allylated calixarene with para-substituent has no occurrence of Claisen rearrangement upon heating, and its crosslinking reaction proceeded at 210–230 °C (much lower than allylated phenolic compounds like Bisphenol-A and phenol-formaldehyde resin).
2. For allylated p-methylcalixarene, nanopore conformation cannot be retained even before thermal cure, due to the disappearance of hydrogen bonds and low steric effect of methyl groups.
3. For allylated p-tert-butylcalixarene, nanopore conformation can be well maintained once the thermal curing temperature is not higher than 130 °C, but at higher curing temperature of 200 °C nanopores will be destroyed and exhibited a quite weak diffraction peak in SAX profile.
4. For allylated p-phenylcalixarene, nanopore conformation can be retained at uncured and high-temperature cured materials, besides the diffraction peak of nanopores shifted to lower position in SAX profile.

5. For allylated calixarene, the thermally cured resin with well-defined nanopores could be realized in the case of a comparably low thermally curing temperature or high steric effect of big substituent on para-sites of phenolic rings.

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