Polymer Vol. 39 No. 16, pp. 3821–3826, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

PII: S0032-3861(97)10377-9

Syntheses and characterizations of three vinyl copolymers containing pendant calix[4]arenes

Michael T. Blanda* and Eba Adou
Department of Chemistry, Southwest Texas State University, San Marcos, TX 78666, USA

(Received 28 March 1997; revised 3 November 1997; accepted 12 November 1997)

Three new copolymers containing pendant calix[4]arene units have been synthesized via radical initiated reactions involving a vinylic calix[4]arene monomer with methylacrylate, acrylonitrile, and styrene. The calix[4]arene monomer was locked into tie cone conformation by appending four ethoxyethyl groups to its lower rim. The upper rim of the calix[4]arene monomer, which was the site of polymerization, was monofunctionalized with a modified acrylate ester moiety. A seven atom spacer group was incorporated between the bulky calixarene core and the acrylate moiety in order to minimize steric interactions which proved to impede the polymerization. The copolymers were designed to take advantage of the well-established binding interactions of calixarenes with neutral molecules and ions. The ultimate goal of this project is to develop materials that are suitable for incorporation into chemical sensor devices such as ion-specific electrodes, semipermeable membranes and quartz microbalances. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: calixarenes; polymers; pendant)

INTRODUCTION

Calix[4]arenes are cyclic tetramers of *t*-butyl phenol and formaldehyde which can be synthetically manipulated to assume rigid, cone-like structures. The cone conformation is characterized as having an upper rim, defined by the para positions of the aromatic rings and a lower rim, defined by the phenolic oxygen atoms. This conformation of calix[4]arenes is capable of binding neutral molecules inside the cavity or metal ions via the oxygen atoms at the lower rim (see *Figure 1*)[1].

Herein we wish to report a new application for the well-established binding properties of calix[4]arenes that involves incorporating them into polymers. These new polymers may then be processed into materials suitable for chemical sensor devices such as ion-selective electrodes and filtration/extraction membranes. Previously reported sensor devices based on calixarenes have been fabricated by blending the calixarene molecules into polymer melts or other membrane composites[2–4]. The same blending technique has been used to incorporate calixarenes into polyvinyl chloride and polystyrene to improve their light and thermal stabilities[5]. Blending methods have several drawbacks including non-uniform ordering of the calixarene units, leaching, and difficulty in reproducing a given set of properties in the blend. Therefore, calixarene-based polymers are a significant improvement in that they will eliminate those problems mentioned. Calixarene-based polymers have just begun to receive attention, and of the few reported in the literature, the site of polymerization is on the lower rim of the calixarene molecules[6–9]. Based on recently available synthetic methodologies, we decided to append the calixarenes to the polymer backbone via their upper rim. The method of incorporation involves radical copolymerization of a monofunctionalized calix[4]arene acrylate ester with methylacrylate using AIBN as the initiator. A representation of the polymer is shown in *Figure 2*.

MONOMER DESIGN AND SYNTHESIS

The scarcity of calixarene-based polymers is, in part, due to the difficulty in synthesizing rationally designed monomers. Recently, however, synthetic methodologies have been developed which permit regioselective functionalization of the upper rim of calix[4]arenes and these methods were employed in synthesizing the calixarene monomer used in our copolymerization experiments. The monomer was derived from the principal starting material, 25,26,27,28-tetraethoxyethyl calix[4]arene **2**[10–12]. This compound was readily available starting from the parent *t*-butyl calix[4]arene **1** (see *Figure 3*) which was prepared from the procedures outlined by Gutsche *et al.*[13].

The next step in the synthesis (see *Figure 4*) involved selective formylation of the upper rim of the calixarene by treatment with dichloromethyl methyl ether in the presence of tin (IV) chloride followed by hydrolysis of the geminal dichloride[10–12]. The formylation reaction provided a mixture of mono- and dialdehydes which were both used in the production of monomer compounds. The polymers derived from the dialdehyde compound will be described in a later communication. The mixture of mono- and dialdehydes was not separated, but instead was reduced to the corresponding alcohol mixture, which was easily separated on silica gel to provide gram quantities of the monoalcohol **3**.

The monoalcohol **3** was then converted into to the monoallyl ether **4** (see *Figure 5*) by deprotonation of the alcohol with NaH followed by treatment with allyl bromide. Initial copolymerization attempts between **4** and

---

* To whom correspondence should be addressed

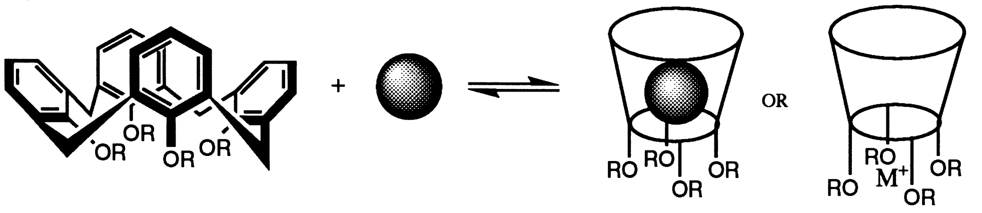

Figure 1 Calixarene host with metal ion or neutral guests forming exo- and endocavity complexes

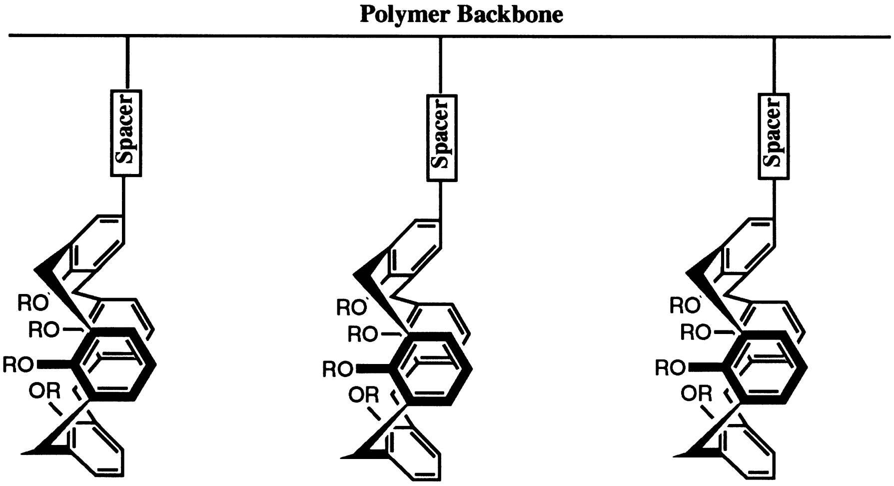

Figure 2 Stylized depiction of pendant calixarene-containing polymers

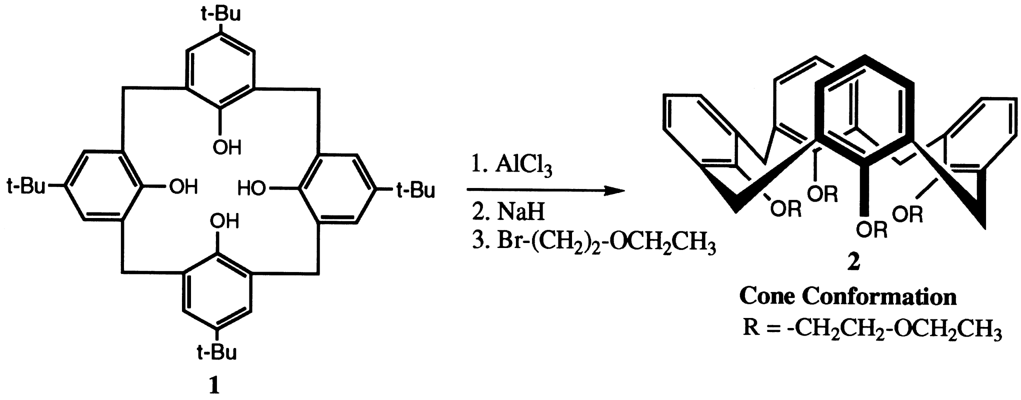

Figure 3 Synthesis of tetraethoxyethyl calixarene in the cone conformation

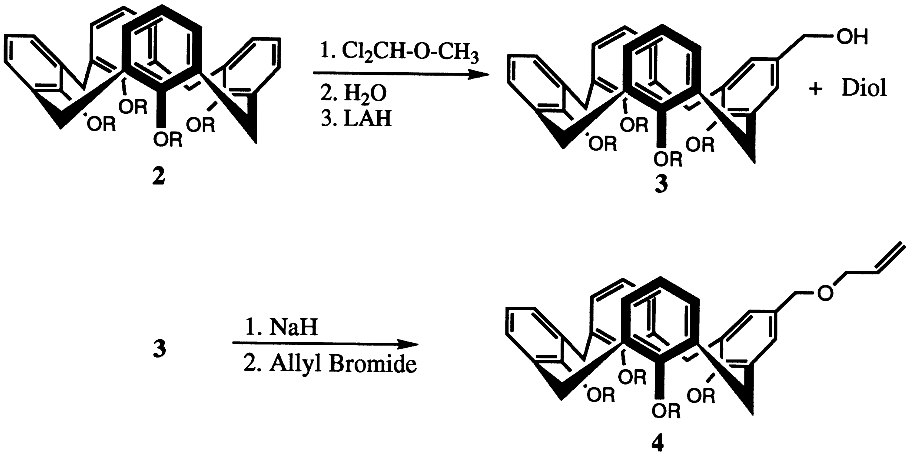

Figure 4 Synthetic schemes for the monoalcohol and monoallyl functionalized precursors **3** and **4**

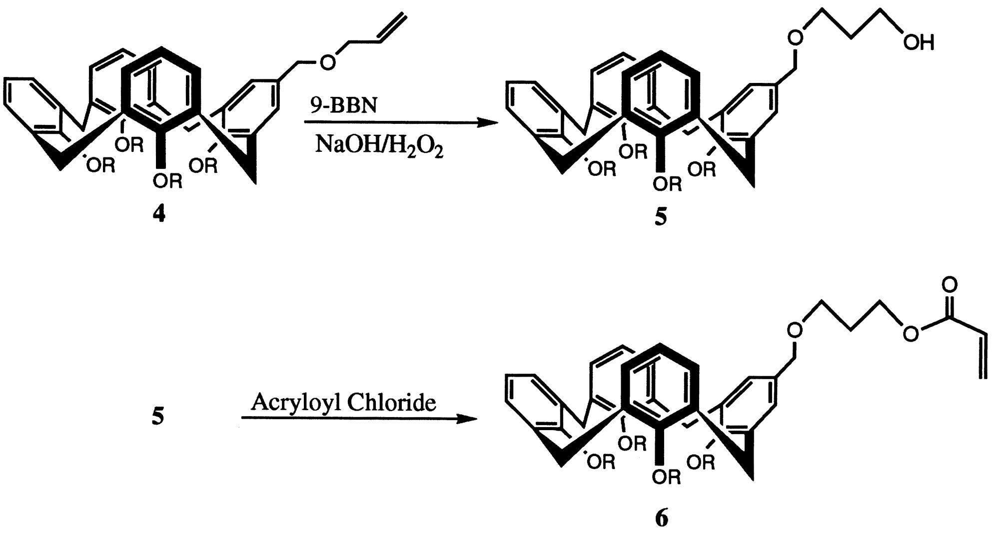

Figure 5 Syntheses for the ‘extended’ monoalcohol precursor **5** and the calixarene monomer **6**

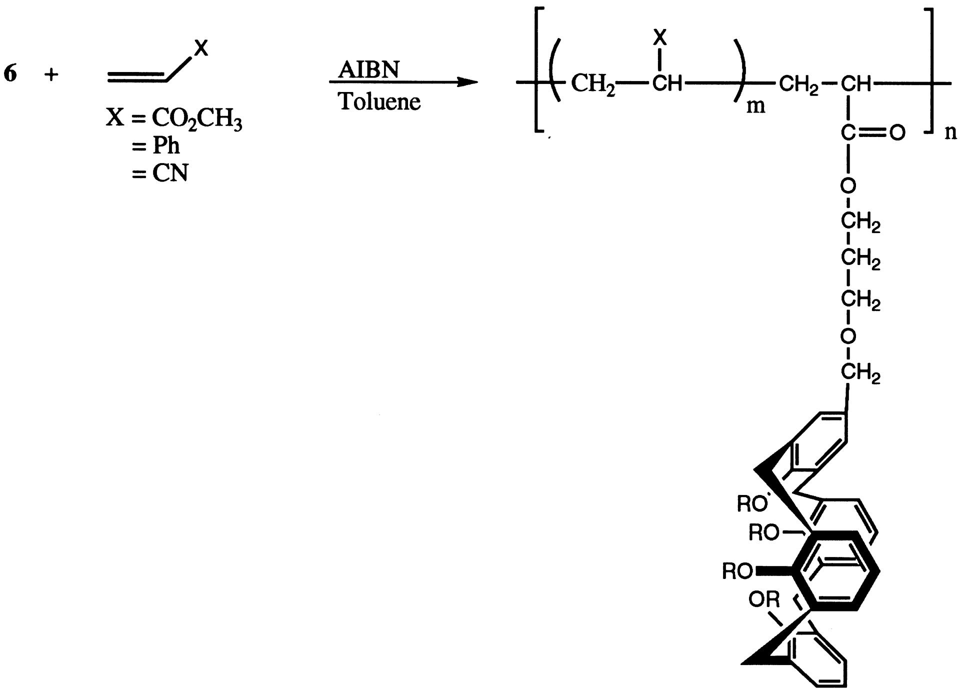

Figure 6 Syntheses of the three vinyl copolymers

methylacrylate yielded a short oligomer with an inherent viscosity of 0.06 dL/g. This result suggested that removal of the site of polymerization away from the bulky calixarene moiety may improve the degree of polymerization. Furthermore, it was rationalized that the reactivity of the carbon–carbon double bond of the calixarene monomer should also be enhanced to match that of the methylacrylate. In order to achieve both of these goals, the monoallyl ether was then transformed into the extended monoalcohol **5** via hydroboration with 9-BBN followed by oxidation of the alkyl borane with hydrogen peroxide and base[14]. The acrylate ester monomer **6** was then synthesized by coupling the extended monoalcohol with acryloyl chloride (see *Figure 6*).

POLYMER SYNTHESES AND CHARACTERIZATIONS

The copolymerization reactions involving monomer **6** with methylacrylate, styrene and acrylonitrile were conducted in sealed vials using dry degassed toluene as the solvent and AIBN as the radical initiator. From preliminary results, it was determined that a 1:100 ratio of AIBN to calixarene monomer resulted in the highest inherent viscosity for the polymers. Furthermore, different ratios of calixarene monomer and the other three vinylic monomers were employed to obtain the highest degree of polymerization and molecular weight. The proton NMR spectra for all of the copolymers clearly illustrated that both monomers were, indeed, incorporated into the repeating unit, since signals unique to both monomers were observed in the copolymer. Furthermore, the signals for the vinylic hydrogens from each monomer were absent, indicating that the reactions were completed within 12 h. The percent composition of each copolymer was determined from integration of signals unique to each monomer (**6** and the vinyl monomer) in the proton NMR spectra. The average molecular weights of the methylacrylate and styrene copolymers were determined by

Table 1 Radical copolymerization of **6** and vinyl monomers[a,b,c]

Monomers (mol %)			Polymer yield (%)	Polymer composition[d] M_1/M_2
Experiment no.	**6** M_1	Vinyl monomer M_2		
1	25	MA, 75	85	1/3
2	9	MA, 91	93	1/16
3	25	ST, 75	75	1/3
4	9	ST, 91	84	1/8
5	25	AN, 75	50	1/3
6	9	AN, 91	63	1/11

[a] All reactions were initiated with 1.0 mol% of AIBN.
[b] Reactions were conducted at 65°C.
[c] Reactions times were 12 h.
[d] Determined by ^1H-NMR.

Table 2 Physical properties of copolymers

Copolymer	Inherent viscosity (dL/g)[a]	TGA[b] (°C)	Tg (°C)	Average molecular wt. (g/mol)[c]
MA 1:3	0.17	377	—	37 000
MA 1:10	0.37	376	81	171 000
PS 1:3	0.18	377	—	45 000
PS 1:10	0.30	371	84	53 000
AN 1:3	0.17	341	—	na[d]
AN 1:10	0.28	343	76	na[d]

[a] Measured in chloroform.
[b] 10% weight loss in nitrogen.
[c] Measured against polystyrene.
[d] Could not be determined due to insolubility in THF.

size exclusion chromatography (SEC) measured against polystyrene standards. The molecular weights for copolymers derived from acrylonitrile could not be determined using this method since they were not soluble in THF. The copolymers are assumed to be atactic, with the pendant calixarenes randomly oriented on either side of the polymer backbone. *Table 1* and *Table 2* summarize the experimental conditions, yields, and physical data for each copolymer. The inherent viscosities for the copolymers were determined using an Ostwald viscometer with chloroform as the solvent[15].

COPOLYMERIZATION WITH METHYLACRYLATE

Initially, reaction mixtures containing 1:1, 2:1, 3:1 and 10:1 ratios of methylacrylate to calixarene were investigated. Oligomeric products with inherent viscosities of 0.06 and 0.11 dL/g, respectively, were obtained with the 1:1 and 2:1 mixtures, while higher molecular weight polymers were obtained with the 3:1 and 10:1 mixtures (see *Table 1*). The average molecular weights for the two copolymers were found to be 37 000 and 171 000 g/mol, respectively. These values represent the average molecular weight of each copolymer since there is a high degree of dispersion in each copolymer. In fact, the range of molecular weights obtained in the 3:1 mixture was 315 000–4300 g/mol, while that for the 10:1 mixture was 1.6 million–10 000 g/mol. This is one of the highest molecular weights measured for any calixarene-containing polymer. Such a high molecular weight is attributed to the enhanced reactivity of the carbon–carbon double bond in both monomers (**6** and methylacrylate).

While the reactivity ratio of **6** and methylacrylate is not strictly known, it is assumed to be close to 1 based on the comparisons of reactivity ratios of methylacrylate with ethylacrylate (0.92/1.08)[16]. The monomer **6** may be described as an '*n*-propyl acrylate' since there is a three carbon spacer between the acrylate moiety and the calixarene unit. This assumption would predict that the ratio of each monomer in the polymer would be similar to that in the reaction mixture, and indeed this is the case (see *Table 1*). While we have demonstrated that **6** can homopolymerize to a certain degree (see below), the average molecular weight of the 'homopolymer' was only approximately 6000 g/mol (hexamer). Furthermore, the GPC analyses of the copolymers was conducted using a UV detector which was set to 280 nm. Since there is no aromatic chromophore in the methylacrylate monomer, the observed signal must reflect the presence of the calixarene monomer. Even though the signals show a large degree of dispersion, there is little doubt that the copolymer has a significant amount of **6** (10–33%) which is more or less evenly distributed in the copolymer. We feel that these arguments also apply to the copolymers with styrene and acrylonitrile.

COPOLYMERIZATION WITH POLYSTYRENE

The morphology of the polystyrene copolymers was more crystalline than that of the methylacrylate copolymers. The average molecular weights for the two copolymers were found to be 45 000 and 54 000 g/mol, respectively. Again, there was a high degree of dispersion in the samples and the molecular weight ranges for each mixture were calculated to be 324 000–10 000 g/mol for the 3:1 mixture and 980 000–7500 g/mol for the 10:1 mixture.

COPOLYMERIZATION WITH ACRYLONITRILE

The two copolymers obtained by reacting **6** with 3 and 10 mol equivalents of acrylonitrile were less soluble than the those obtained with either methylacrylate or styrene. However, these copolymers were soluble to in $CDCl_3$ allowing for NMR analyses and viscosity measurements. The inherent viscosities of 0.17 and 0.28 dL/mL (for 3:1 and 10:1 mixtures) were similar to those determined for the methylacrylate and styrene mixtures at the same ratios, thus it is reasonable to assume that these two copolymers have similar average molecular weights and molecular weight ranges. It may be further reasoned that the molecular weight ranges may actually be in between the ranges found for the methylacrylate and styrene copolymers, since the reactivity of the carbon–carbon double bond in acrylonitrile is less than that of methylacrylate and greater than that of styrene in similar radical reactions. The yields for the acrylonitrile copolymers were somewhat less at 50% and 63%, respectively, possibly due to the insoluble nature of the copolymers. As the polymer chains grew in length, they became less soluble and precipitated from the toluene solution.

HOMOPOLYMERIZATION OF **6**

Attempts were made to homopolymerize the calixarene monomer **6** under the same conditions as were used in the copolymer reactions. Unfortunately, only oligomeric products were produced with inherent viscosities of 0.06 dL/g. This result was obtained presumably due to the steric interactions that occurred between the bulky calixarene moieties in the absence of any spacer group.

EXPERIMENTAL SECTION

*5-(1-propenyloxymethyl)-25,26,27,28-tetra(2-ethoxyethyl) calix[4]arene (***4***)*

Compound **3** (6 g, 8 mmol) and allyl bromide (2.6 mL, 29.9 mmol) were dissolved in 300 mL of dry DMF. To this solution was added NaH (1.6 g, 32 mmol) which was washed with hexanes to remove the mineral oil. The solution was then heated to 80°C and stirred for 24 h. The solvent was then removed under reduced pressure and the residue was taken up in 300 mL of ethylacetate and 300 mL of water was added. The organic layer was separated and again washed with 2 × 300 mL of water and once with 300 mL of brine. The organic layer was then dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product. The product was chromatographed on silica gel (hexanelethylacetate: 70/30) to yield 5.0 g (80%) of **4** as a white semi-solid; mp 87–90°C. ^1H-NMR $CDCl_3$ δ 6.8–6.4 (*m*, 11H), 6.0–5.6 (*m*, 2H), 5.24–5.05 (*m*, 1H), 4.48 and 3.18 (*AB* quartet, 8H), 4.2–4.0 (*m*, 10H), 3.9–3.6 (*m*, 10H), 3.49 (*q*, 8H), 1.19 (*t*, 12H). $^{13}C-NMR$ $CDCl_3$ δ 156.4, 156.12, 155.72, 135.12, 135.08, 134.92, 134.78, 134.68, 131.49, 128.25, 128.18, 127.99, 127.73, 122.15, 121.91, 116.91, 78.58, 76.99, 75.41, 73.19, 72.97, 71.91, 70.53, 69.61, 66.299 66.25, 30.79, 15.23. Analytically calculated value for $C_{48}H_{62}O_9$: C, 73.64; H, 7.98. Found: C, 73.73; H, 8.06.

*5-(1-hydroxy propyloxy methyl)-25,26,27,28-tetra(2ethoxyethyl)calix[4]arene (***5***)*

Compound **4** (5 g, 6.38 mmol) was dissolved in 150 mL of freshly distilled THF. To this was added dropwise 64 mL, (31.9 mmol) of 9-BBN over a 5 min period. The reaction mixture was then refluxed for 12 h then allowed to cool to room temperature. The resulting organoborane was then oxidized by adding successively 25 mL of absolute ethanol, 8 mL of 6 N NAOH, and 16 mL of 30% hydrogen peroxide. The solution was then heated to 50°C and stirred for 12 h. The reaction mixture was cooled to room temperature and the aqueous layer was saturated with potassium carbonate. The organic layer was separated and dried over anhydrous potassium carbonate, filtered and concentrated under reduced pressure to provide the product as a viscous oil. The oil was chromatographed on silica gel (hexanelethylacetate: 70/30) to yield 3.5 g (68%) of compound **5**. ^1H-NMR $CDCl_3$ δ 6.65–6.49 (*m*, 11H), 4.50 and 3.12 (*AB* quartet, 8H), 4.2–4.0 (*m*, 12H), 3.9–3.6 (*m*, 10H), 3.49 (*q*, 8H), 1.74 (*m*, 2H), 1. 19 (*t*, 12H). $^{13}C-NMR$ $CDCl_3$ δ 156.43, 156.06, 155.68, 135.07, 134.69, 131.32, 129.17, 127.92, 127.43, 122.10, 121.79, 73.16, 72.91, 69.56, 68.59, 66.22, 61.62, 31.99, 30.76, 15.17. Analytically calculated value for $C_{48}H_{64}O_{10}$: C, 71.98; H, 8.05. Found: C, 72.19; H, 8.21.

*5-(1-acryloyloxy propyloxy methyl)-25,26,27,28-tetra(2-ethoxyethyl)calix[4]arene (***6***)*

In a three neck round bottom flask fitted with an addition funnel was placed a solution containing 3 g (3.75 mmol) of compound **5** dissolved in 60 mL of freshly distilled THF. To this solution was added 1.5 mL of triethylamine and the solution was then cooled to 0°C. A second solution containing 3.1 mL (37.5 mmol) of acryloyl chloride dissolved in 20 mL of THF was prepared and placed in the addition funnel fitted on to the reaction vessel. This solution was added dropwise to the calixarene solution over a 10 min period while maintaining the reaction temperature at 0°C for 1 h. The ice bath was removed and the reaction was allowed to warm to room temperature and stirred for an additional 24 h. The reaction mixture was concentrated under reduced pressure and the resulting liquid was poured into 100 mL of water. The aqueous mixture was then extracted with 3 × 100 mL of $CHCl_3$. The combined organic layers were washed with water then brine and dried over $MgSO_4$. The solution was filtered and concentrated under vacuum to yield a viscous oil. The oil was chromatographed on silica gel (hexaneslethylacetate: 70130) to yield 1.98 g, (62%) of the acrylate ester **6**. ^1H-NMR $CDCl_3$ δ 6.66–6.49 (11, H), 6.44–6.18 (*m*, 2H), 6.09–5.92 (*m*, 1H), 4.50 and 3.12 (*AJB* quartet, 8H), 4.2–4.0 (*m*, 12H), 3.9–3.6 (*m*, 10H), 3.49 (*q*, 8H), 1.87 (*m*, 2H), 1.21–1.19 (*t*, 12H). $^{13}C-NMR$ $CDCl_3$ δ 166.04, 156.48, 156.11, 155.65, 135.14, 134.72, 134.66, 131.53, 130.34, 129.52, 129.21, 127.95, 127.45, 122.12, 122.81, 73.18, 72.96, 69.58, 66.23, 61.88, 30.79, 29.98, 15.21. Analytically calculated value for $C_{51}H_{66}O_{11}$: C, 71.64; H, 7.78. Found: C, 71.64; H, 7.83.

POLYMERIZATION REACTIONS

Copolymerization reactions utilizing the calixarene monomer **6** with three and 10 molar equivalents of the vinyl monomers were conducted. In all reactions, 1 mL of dry toluene was used as the solvent and AIBN was used as the initiator. Below are the representative experimental conditions for the three types of vinyl monomers.

COPOLYMERIZATION WITH METHYLACRYLATE

The calixarene ester monomer **6** (0.332 g, 0.47 mmol) and 7 mg, (0.043 mmol) of AIBN were placed into a vial. To this was added 10 molar equivalents (0.349 mL, 3.88 mmol) of methylacrylate and 1 mL of toluene. The contents of the vial were degassed by performing three successive freeze–pump–thaw cycles and the vial was sealed under vacuum. The vial was heated in an oil bath to 70°C for 12 h. The vial was opened and the reaction mixture was poured into methanol to precipitate the product and remove any unreacted methylacrylate. The product was filtered and dried under vacuum to provide 0.621 g (93%) of the copolymer. IR (KBr) 2972 cm^{-1} (C–H Ar), 1738 cm^{-1} (C=O) ^{1}H – NMR CDCl$_3$ δ 6.62–6.51 (11, H), 4.50 and 3.12 (*AB* quartet, 8H), 4.2–4.0 (*m*, 30H), 3.9–3.6 (*m*, 10H), 3.49 (*q*, 8H), 2.33 (*bs*, 4H) 1.70 (*m*, 10H), 1.21–1.19 (*t*, 12H).

COPOLYMERIZATION WITH STYRENE

The calixarene ester monomer **6** (0.397 g, 0.465 mmol) and 7 mg of AIBN were placed into a vial. To this was added 10 molar equivalents (0.532 mL, 4.65 mmol) of styrene and 1 mL of toluene. The vial was sealed as above and heated to 70°C for 12 h. The vial was opened and the solution was poured into methanol to precipitate the polymer. The polymer was filtered and dried under vacuum to yield 0.74 g (84%) of the copolymer. IR (KBr) 2972 cm^{-1} (C–H Ar), 1738 cm^{-1} (C=O) ^{1}H – NMR CDCl$_3$ δ 7.25 (*bs*, 23H) 7.03–6.48 (*m*, 27H), 4.57 and 3.21 (AB quartet, 8H), 4.13–4.02 (*m*, 12H), 3.89–3.66 (*m*, 10H), 3.49 (*q*, 8H), 1.72 (*bs*, 36H), 1.20 (*t*, 12H).

COPOLYMERIZATION WITH ACRYLONITRILE

The calixarene ester monomer **6** (0.315 g, 0.369 mmol) and 7 mg, (0.041 mmol) of AIBN were placed into a vial. To this was added 0.243 mL (3.69 mmol) of acrylonitrile and 1 mL of toluene. The vial was sealed as above and heated to 70°C for 12 h. The vial was opened and the solution was poured into methanol to precipitate the polymer. The polymer was filtered and dried under vacuum to yield 0.511 g (63%) of the copolymer. IR (KBr) 2972 cm^{-1} (C–H Ar), 1738 cm^{-1} (C=O) ^{1}H – NMR CDCl$_3$ δ 6.56–6.45 (*m*, 11H), 4.57 and 3.21 (AB quartet, 8H), 4.13–4.02 (*m*, 12H), 3.89–3.66 (*m*, 10H), 3.49 (*q*, 8H), 2.18–1.28 (*bs*, 36H), 1.12 (*t*, 12H).

ACKNOWLEDGEMENTS

M.T.B. thanks the Robert A. Welch Foundation, Petroleum Research Fund and The Research Corporation for financial support. M.T.B. also thanks Drs John W. Fitch and Eric Fossum for helpful discussions.

REFERENCES

1. C. D., Gutsche, *Calixarenes, Monographs in Suprainolecular Chemistry*, Vol. 1, ed. Stoddart, J. F., The Royal Society of Chemistry, Cambridge, 1989.
2. Kimura, K., Miura, T., Matsuo, M. and Shono, T., *Analyt. Chem.*, 1990, **62**, 1510.
3. Chan, W. H., Shiu, K. K. and Gu, X. H., *Analyst*, 1993, **118**, 863.
4. Chan, W. H., Cai, P. X. and Gu, X. H., *Analyst*, 1994, **119**, 1853.
5. Seiffarth, K., Shulz, M., Gormar, G. and Bachmann, J., *Polymer Deg. Stab.*, 1989, **24**, 73.
6. Arrigan, D. W. M., Svehla, G., Harris, S. J. and McKervey, M. A., *Analyt. Proc.*, 1992, **29**, 27.
7. Deligoz, H., Tavasli, M. and Yilmaz, M., *J. Polym. Sci. Part A: Polym. Chem.*, 1994, **32**, 2961.
8. Harris, S. J., Barrett, G. and McKervey, M. A., *J. Chem Soc. Chem. Commun.* 1991, 1224.
9. Kawabata, H., Aoki, M., Murata, K. and Shinkai, S., *Supamol. Chem.*, 1993, **2**, 33.
10. van Loon, J. D. and Reinhoudt, D. N., *Org. Prep. Proc. Int.*, 1992, **24**, 437. and references cited therein.
11. van Loon, J. D., Arduini, A., Coppi, L., Verboom, W., Pochini, A., Ungaro, R., Harkema, S. and Reinhoudt, D. N., *J. Org. Chem.*, 1990, **55**, 5639.
12. Arduini, A., Manfredi, G., Pochini, A., Sicuri, A. R. and Ungaro, R., *J. Chem. Soc. Chem. Commun.* 1991, 936.
13. Gutsche, C. D. and Pagoria, P. F., *J. Org. Chem.*, 1985, **50**, 5795.
14. Brown, H. C., Knights, E. F. and Scouten, C. G., *J. Am. Chem. Soc.*, 1974, **96**, 7765.
15. Allcock, H. R. and Lampe, F. W., in *Contemporary Polymer Chemistry*. Prentice Hall, Englewood Cliffs, NJ, 1981, pp. 378–404.
16. Brandup, J. and Immergut, E. H. (eds.), *Polymer Handbook*, 2nd edn. Wiley, New York.