Hydrogen Bonding in Trivinyl Monomers: Implications for Inclusion Complexation and Polymerization

Sunita S. Satav,[†] Rohini N. Karmalkar,[†] Mohan G. Kulkarni,*[,†] Nagaraju Mulpuri,[‡] and G. Narahari Sastry[‡]

Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411 008, India, and Molecular Modeling Group, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received October 18, 2006; Revised Manuscript Received January 9, 2007

ABSTRACT: Trimethylolpropane trimethacrylate (TMPTMA) formed a 1:2 inclusion complex (IC) with β-cyclodextrin (β-CD). Polymerization of the complex resulted in a soluble, linear polymer containing two pendant unsaturations per repeat unit since the methacryloyl groups included in the β-CD cavity did not react with the growing radical chain. Trimethylolpropane triacrylate (TMPTA) formed a 1:1 complex with β-CD. Yet a soluble polymer containing two pendant unsaturations per repeat unit was obtained. Computational analysis confirmed that in TMPTA hydrogen bonding between C−H···O═C brings two acryloyl groups in close vicinity of one another. As a result, both acryloyl groups were included in the same β-CD cavity. Trimethylolpropane diacrylate 4-vinylbenzoate (TMPDAVB) once again formed 1:2 IC as a result of disruption of hydrogen bonds between two acryloyl groups. The study highlights that an understanding of the composition of the IC is more important than its stoichiometry alone.

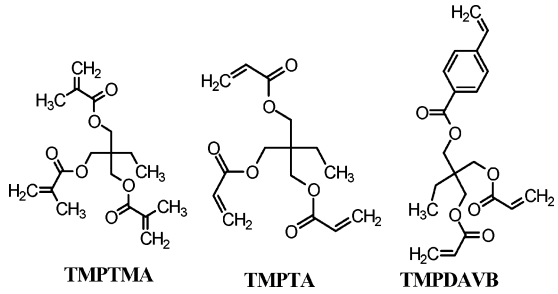
Introduction

Polymer architecture governs its properties and performance.[1] Synthetic approaches to develop soluble polymers, which can be cross-linked in a subsequent step, are increasingly being explored in view of their applications in electronics, optoelectronics, molecular imprinting, microlithography, and nanotechnology.[2] This has been hitherto achieved by (a) conjugation of vinyl monomers with polymers containing pendant functional groups[2a−d] and (b) copolymerization with cross-linkers containing multiple unsaturated groups differing in reactivity.[2e] The first approach is limited by the choice of monomers while the latter is limited by the choice of cross-linkers. Clearly there is a need for a single step method for the synthesis of soluble polymers containing unsaturation, which can be cross-linked in a subsequent step and is independent of the nature of the monomer as well as the cross-linkers.

Supramolecular complexes, especially the ones comprising cyclodextrin (CD), have led to the development of a wide range of polymer architectures such as polyrotaxanes and pseudopolyrotaxanes.[3] Chen et al.[4] exploited inclusion complexes (ICs) comprising CDs to synthesize linear polymers by polycondensation of 1-(2-aminoethyl)piperazine−CD IC and divinylsulfone, which in the absence of the CD formed hyperbranched structures. Recently we reported that the divinyl monomer ethylene glycol dimethacrylate (EGDMA) formed 1:1 IC with β-CD, and selective polymerization of free methacryloyl group led to a linear, soluble polymer containing a pendant methacryloyl group per repeat unit, as the methacryloyl group included in the β-CD cavity did not react with the growing radical chain.[5] These pendant methacryloyl groups can be subsequently reacted by thermal or UV irradiation to yield cross-linked polymers.

In view of applications of polymers, which are soluble and need to be more densely cross-linked, we extended the investigations to the selective polymerization of trivinyl monomers (Schemes 1 and 2). It was observed that the trivinyl monomer trimethylolpropane trimethacrylate (TMPTMA) formed 1:2 IC with β-CD. This is analogous to EGDMA, which formed 1:1 complex with β-CD, leaving one of the methacryloyl groups free for polymerization. On the other hand, trimethylolpropane triacrylate (TMPTA) formed 1:1 IC. Surprisingly, polymerization of both complexes led to soluble polymers containing two unreacted double bonds per repeat unit.

Scheme 1. Chemical Structures of Trivinyl Monomers, TMPTMA, TMPTA, and TMPDAVB



Computational analysis of TMPTMA-β-CD IC revealed that the two methacryloyl groups were included in two different β-CD cavities. In the case of TMPTA-β-CD IC, hydrogen-bonding interactions between C−H···O═C of two acryloyl groups brought them close enough to be included in the same β-CD cavity. Substitution of one of the acrylate groups in TMPTA by 4-vinyl benzoate to form trimethylolpropane diacrylate 4-vinylbenzoate (TMPDAVB) disrupted the intramolecular hydrogen bonding between two acryloyl groups. As a result, TMPDAVB formed a 1:2 IC, wherein each acryloyl group was included in one β-CD cavity.

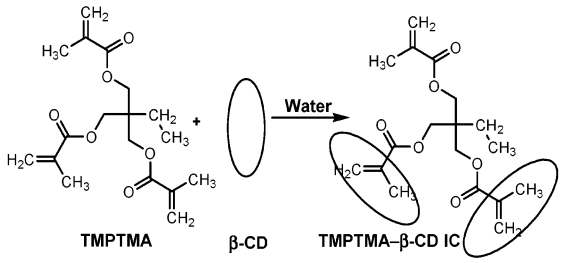
The structures of ICs of TMPTMA, TMPTA, and TMPDAVB with β-CD were investigated by instrumental techniques such as ^{1}H NMR, ^{13}C CP/MAS, FTIR, XRD, and molecular modeling analysis. It is demonstrated that the stoichiometry of IC is governed by the disposition of the vinyl groups, which in turn is governed by hydrogen bonding within the cross-linker.

* Corresponding author. E-mail: mg.kulkarni@ncl.res.in.
[†] National Chemical Laboratory.
[‡] Indian Institute of Chemical Technology.

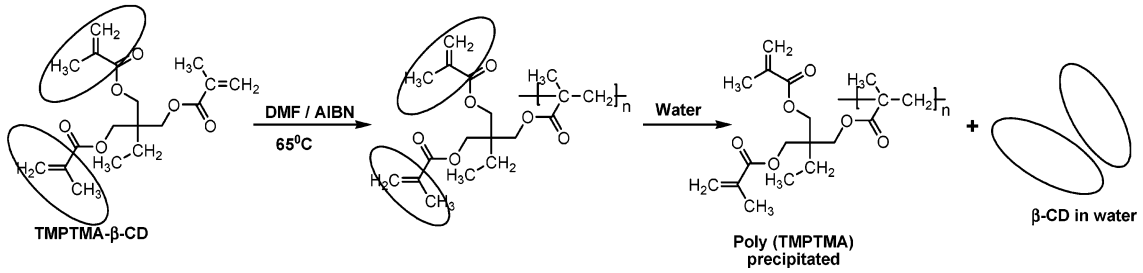
10.1021/ma062397i CCC: $37.00
Published on Web 02/15/2007

Scheme 2. Synthesis of Soluble Polymer from Trivinyl Monomer

a. TMPTMA-β-CD (1:2) IC: Preparation



b. TMPTMA-β-CD (1:2) IC: Polymerization



Experimental Section

Materials. Trimethylolpropane trimethacrylate (TMPTMA) and trimethylolpropane triacrylate (TMPTA) were obtained from Aldrich. Trimethylolpropane diacrylate 4-vinylbenzoate (TMPDAVB) was synthesized by stepwise esterification of trimethylolpropane with 4-vinylbenzoyl chloride followed by acryloyl chloride. β-Cyclodextrin (β-CD) was purchased from SD Fine Chemicals. The initiator azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol (MeOH). The solvents *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chloroform ($CHCl_3$), methyl ethyl ketone (MEK), and MeOH were purchased from Merck Chemicals. The deuterated solvents $CDCl_3$ and DMSO-d_6 were obtained from Aldrich.

Measurements. ^{1}H NMR spectra were recorded on Bruker DRX 500 MHz NMR spectrometer. The solid-state ^{13}C CP/MAS NMR spectra of β-CD and ICs were measured on a Bruker DRX 500 MHz NMR spectrometer at 125 MHz with a sample spinning rate of 8 kHz.

FT-IR spectra were recorded on Perkin-Elmer Spectrum One. The spectra were recorded at frequencies from 4000 to 450 cm^{-1}. The resolution was 4 cm^{-1}. ICs were mulled in nujol, and the spectra of polymers were obtained in $CHCl_3$. Respective solvents were used as reference.

Powder X-ray diffraction (XRD) patterns of ICs were recorded on a Rigaku Dmax 2500 diffractometer with Cu Kα (1.541 Å) radiation (40 kV, 100 mA). Powder samples such as β-CD and ICs were mounted on a sample holder and scanned with a step size of 0.05° in the range $2\theta = 5-40°$.

Molecular weights of the polymers were measured by gel permeation chromatography (GPC) using two polystyrene−DVB cross-linked gel columns 1 × 60 cm 100 Å and 1 × 60 cm 100 Å from PSS GmbH using THF as eluent at a flow rate of 1 mL min^{-1}.

The light scattering (LS) measurements were carried out on a light scattering photometer Malvern model 4700 at 25 °C in THF with the laser operating at 488 nm. The d*n*/d*c* (0.11 mL/g) for poly(TMPTMA) was determined in THF at 25 °C using a Brice-Phoenix differential refractometer.

The intrinsic viscosity of polymer solutions in THF was measured at 25 °C using an Ubbelohde capillary viscometer.

Differential scanning calorimetric (DSC) measurements were performed under nitrogen at a flow rate of 50 mL min^{-1} on a differential scanning calorimeter (TA Instruments, model Q-10). Polymer sample was heated from −50 to 150 °C at 10 °C min^{-1} and scanned to calculate the glass transition temperature (T_g) of the polymer in subsequent heating cycles.

Synthesis of IC. 11.35 g (0.01 mol) β-CD was dissolved in 615 mL of water. To this, 1.692 g (0.005 mol) of TMPTMA or 2.96 g (0.01 mol) of TMPTA or 1.86 g (0.005 mol) of TMPDAVB was added and stirred for 48 h at room temperature. The complex slowly precipitated out. It was filtered and washed with distilled water followed by petroleum ether to remove uncomplexed β-CD and trivinyl monomer respectively. The stoichiometry of the ICs was determined using ^{1}H NMR, and the yields were calculated on the basis of the amount of trivinyl monomers and β-CD used for complexation.

Yields: TMPTMA-β-CD = 65.70%, TMPTA-β-CD = 77.53%, and TMPDAVB-β-CD = 83.19%.

The ICs of TMPTMA and TMPTA with β-CD were also prepared varying the molar feed ratio of trivinyl monomer to β-CD under identical conditions to study the effect of feed composition on the stoichiometry of ICs.

^{1}H NMR (DMSO-d_6). TMPTMA-β-CD IC, δ [ppm]: 0.87 (3H, CH_2-CH_3 of TMPTMA), 1.52 (2H, CH_2-CH_3 of TMPTMA), 1.85 (9H, CH_3 adjacent to vinyl group of TMPTMA), 4.11 (6H, OCH_2 of TMPTMA), 5.67 and 6.01 (6H, vinyl protons of TMPTMA), 5.72 (7H, C_2-OH of β-CD), 5.71 (7H, C_3-OH of β-CD), 4.49 (7H, C_6-OH of β-CD), 4.83, (7H, C_1-H of β-CD), 3.30 (7H, C_2-H of β-CD), 3.61 (C_3-H of β-CD), 3.35 (7H,C_4-H of β-CD), 3.53 (C_5-H of β-CD), 3.62 (14H, C_6, H_a and H_b of β-CD).

TMPTA-β-CD IC, δ [ppm]: 0.85 (3H, CH_2-CH_3 of TMPTA), 1.46 (2H, CH_2-CH_3 of TMPTA), 4.0 to 4.12 (6H, OCH_2 of TMPTA), 5.92 to 6.38 (9H, vinyl protons of TMPTA), 5.68 to 5.76 (14H, C_2-OH of β-CD and C_3-OH of β-CD), 4.49 (7H, C_6-OH of β-CD), 4.83, (7H, C_1-H of β-CD), 3.30 (7H, C_2-H of β-CD), 3.61 (C_3-H of β-CD), 3.34 (7H, C_4-H of β-CD), 3.53 (C_5-H of β-CD), 3.63 (14H, C_6, H_a and H_b of β-CD).

TMPDAVB-β-CD IC, δ [ppm]: 0.91 (3H, CH_2-CH_3 of TMPDAVB), 1.55 (2H, CH_2-CH_3 of TMPDAVB), 4.22 to 4.29 (6H, OCH_2 of TMPDAVB), 5.92 to 6.38 (6H, vinyl protons of aliphatic part of TMPDAVB), 5.47, 5.41, and 6.75 to 6.90 (3H, vinyl protons of aromatic part of TMPDAVB), 7.95−7.60 (4H, aromatic proton of TMPDAVB), 5.68 to 5.76 (14H, C_2-OH of β-CD and C_3-OH of β-CD), 4.47 (7H, C_6-OH of β-CD), 4.83 (7H, C_1-H of β-CD), 3.30 (7H, C_2-H of β-CD), 3.61 (C_3-H of

Table 1. Stoichiometry of ICs

	ratio in IC by ^{1}H NMR	
ratio in feed	4.82 δ	4.49 δ
TMPTMA:β-CD		
1:1	1:2.20	1:2.20
1:2	1:2.04	1:2.01
1:3	1:2.11	1:2.13
TMPTA:β-CD		
1:1	1:1.13	1:1.15
1:2	1:1.16	1:1.19
1:3	1:1.10	1:1.10

β-CD), 3.34 (7H, C_4−H of β-CD), 3.53 (C_5−H of β-CD), 3.63 (14H, C_6, H_a and H_b of β-CD).

Polymerization of ICs. Poly(TMPTMA). 1 g (3.83×10^{-4} mol) of IC and 5 mg (3.04×10^{-5} mol) of AIBN were dissolved in 16 mL of DMF, and nitrogen was purged for 10 min. Polymerization was carried out for 16 h at 65 °C. The polymer was precipitated in cold water. The crude polymer was dissolved in THF and reprecipitated in petroleum ether. The polymer was filtered and dried at room temperature.

Polymers of TMPTMA of various molecular weights were prepared by varying initiator concentration in the range 7−15 mol % of monomer and characterized for intrinsic viscosity in THF at 25 °C (see Scheme 2).

Polymerization of TMPTA-β-CD (1:1) IC and TMPDAVB-β-CD (1:2) IC was carried out in an identical manner.

^{1}H NMR ($CDCl_3$). Poly(TMPTMA) δ [ppm]: 0.80−1.59 (3H, CH_2-CH_3, 2H, CH_2-CH_3, 3H, CH_2-CCH_3 on polymer backbone), 1.70 (2H, CH_2-CCH_3, backbone), 1.94 (6H, $CH_2=CCH_3$), 4.16 (4H, OCH_2 adjacent to unreacted vinyl unsaturations), 4.34 (2H, $-OCH_2$ adjacent to polymer backbone), 5.58 (2H, CH_aH_b = CH), 6.10 (2H, CH_aH_b=CH).

Poly(TMPTA) δ [ppm]: 0.85−1.43 (3H, CH_2-CH_3, 2H, CH_2-CH_3), 1.70 (2H, CH-CH_2 backbone), 2.59 (1H, $CH-CH_2$ backbone), 3.52 − 4.58 (6H, OCH_2), 5.88 to 7.54 (6H, $CH=CH_2$)

Poly(TMPDAVB) δ [ppm]: 0.85−1.87 (3H, CH_2-CH_3, 2H, CH_2-CH_3, 2H, CH_2 backbone), 4.25 (4H, OCH_2 adjacent to unreacted vinyl unsaturations) 4.31 (2H, OCH_2 adjacent to polymer backbone), 5.83 to 6.36 (6H, $CH=CH_2$), 7.36−7.49 and (4H, aromatic protons).

Results and Discussion

ICs of Trivinyl Monomers with β-CD. The aqueous solution of β-CD became turbid after addition of trivinyl monomer, indicating formation of ICs as a result of geometrical fit of the monomer into the cavity of β-CD.[6] The precipitated complexes were filtered and thoroughly washed with distilled water and petroleum ether to ensure complete removal of any uncomplexed β-CD and trivinyl monomers, as the presence of adsorbed trivinyl monomer on IC would lead to cross-linking. The complexes were characterized by instrumental methods such as NMR, FTIR, and XRD for stoichiometry, interaction with β-CD, and structure, respectively.

^{1}H NMR Analysis of ICs. The NMR spectroscopy has been extensively used to study the inclusion of guest molecules in β-CD and establish the stoichiometry of ICs formed.[3a,7] Zhao and Beckham[8] reported rapid dethreading of ICs in DMSO because of which the NMR spectrum of the ICs appeared identical to the spectrum of a physical mixture of the two components. This dethreading of trivinyl monomer from β-CD was also confirmed by the polymerization of the ICs in DMSO, which led to cross-linked product, as anticipated. Therefore, the shifts due to formation of ICs were not observed in the spectrum. Yet the integration of the peaks helped establish the stoichiometry of the complex.

The stoichiometry of TMPTMA-β-CD IC was established by integrating the peak at δ 4.16, which corresponds to six

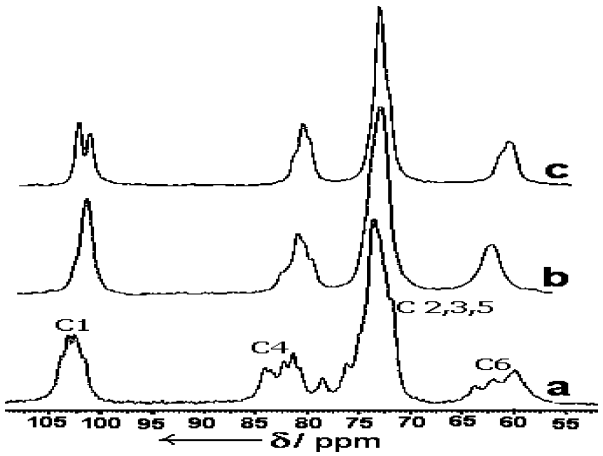


Figure 1. Solid state ^{13}C CP/MAS NMR spectra of (a) β-CD, (b) TMPTMA-β-CD (1:2) IC, and (c) TMPTA-β-CD (1:1) IC.

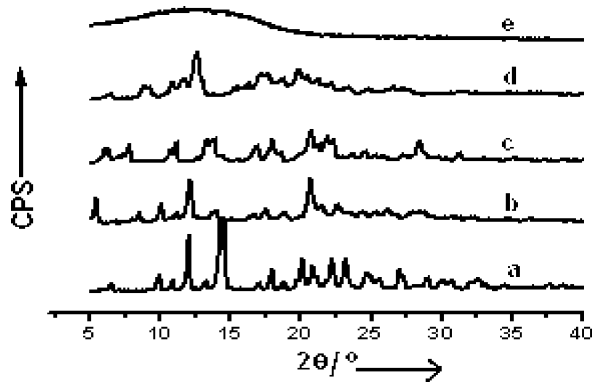


Figure 2. X-ray diffractogram of (a) β-CD, (b) TMPTA-β-CD (1:1) IC, (c) TMPTMA-β-CD (1:2) IC, (d) poly(TMPTMA) before removal of β-CD, and (e) poly(TMPTMA) after removal of β-CD.

protons of TMPTMA (OCH_2), and the peaks at δ 4.49 and 4.82, which corresponds to seven protons of β-CD for (CH_2-OH) and (C_1−H), respectively. The results confirmed formation of 1:2 IC for the system TMPTMA-β-CD. Similar examination for TMPTA and TMPDAVB showed the formation of 1:1 and 1:2 ICs with β-CD, respectively. The results in Table 1 further indicate that TMPTMA molecule always yielded 1:2 IC while TMPTA yielded 1:1 IC irrespective of the feed composition.

^{13}C CP/MAS NMR Analysis of ICs. Solid-state NMR spectra of the ICs provide the evidence for inclusion of guest into the cavity of CD.[3a] ^{13}C CP/MAS solid-state NMR spectra of the TMPTMA-β-CD and TMPTA-β-CD IC shown in Figure 1 displayed well-resolved single peaks for each carbon of all glucose units. Also the peaks at ∼78.59 and ∼101 ppm, corresponding to C_1 and C_4, adjacent to conformationally strained glycosidic linkage, disappeared. These results confirmed symmetrical conformation of glycosidic linkage due to the inclusion of the methacryloyl and acryloyl group of TMPTMA and TMPTA, respectively, within the cavity of β-CD.[3]

FTIR Characterization of ICs. FTIR measurements have been used to demonstrate the presence of both host and guest components and their interactions with each other after the formation of an IC.[3g] The FTIR signals and a shift in the peak positions for ICs and comparison with uncomplexed compounds are summarized in Table 2.

The comparison between the FTIR spectra of free and complexed molecules showed the relative shift in ester carbonyl of trivinyl monomers and the O−H band of β-CD. The FTIR spectrum of TMPTMA-β-CD IC showed a shift from 1722 to 1727 cm^{-1} in ester carbonyl stretching vibrations.[9] The O−H

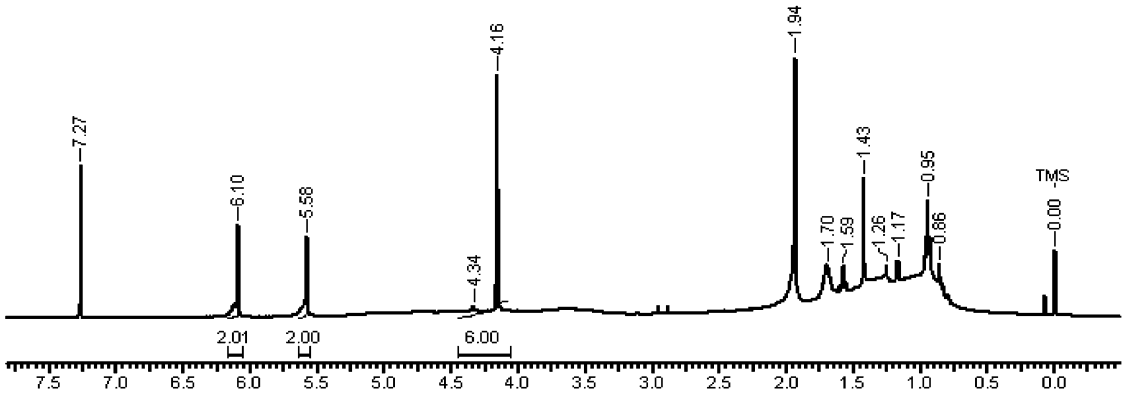


Figure 3. ^{1}H NMR spectrum of poly(TMPTMA) in $CDCl_3$.

Table 2. FTIR Signals in cm^{-1} of ICs, Polymers, and Comparison with the Uncomplexed Compounds (Difference in cm^{-1})

no.	trivinyl monomer	compound	⟩C═O (cross-linker)	O−H (β-CD)
1	TMPTMA	TMPTMA-β-CD	1727 (−5)	3311 (+59)
		poly(TMPTMA) (in presence of β-CD)	1729 (−7)	3338 (+32)
		poly(TMPTMA) (after removal of β-CD)	1720 (+2)	
2	TMPTA	TMPTA-β-CD	1732 (0), 1708 (+24)	3329 (+41)
		poly(TMPTA) (in presence of β-CD)	1738 (−6)	3345 (+25)
		poly(TMPTA) (after removal of β-CD)	1741 (−9), 1732 (0), 1716 (+16)	
3	TMPDAVB	TMPDAVB-β-CD	1733 (+5, −2)	3330 (+40)
		poly(TMPDAVB) (in presence of β-CD)	1731 (+5,0)	3351 (+19)
		poly(TMPDAVB) (after removal of β-CD)	1728 (+10, +5)	

stretching band of β-CD at 3370 cm^{-1} shifted to 3311 cm^{-1} and narrowed as a result of replacement of intramolecular hydrogen bonding in β-CD by intermolecular hydrogen bonding between the guest molecule and β-CD.[3b−h]

In contrast, the FTIR spectrum of TMPTA-β-CD showed the splitting of broad ester carbonyl stretching vibrations of TMPTA. The peak corresponding to ester carbonyl, which is included in the β-CD cavity, appeared at 1708 cm^{-1}, and the carbonyl group not included in the β-CD cavity appeared at 1732 cm^{-1}. The spectrum also showed the presence of two peaks at 1640 and 1616 cm^{-1} for the double bonds, which were attributed to hydrogen-bonded and free acryloyl groups in TMPTA. Thus, the differences in the complexation behavior with β-CD may be attributed to the formation of intramolecular hydrogen bonds in TMPTA and lack of it in TMPTMA. To ascertain whether the disruption of hydrogen bonding in TMPTA restores the formation of 1:2 IC, one of the acrylate groups in TMPTA was replaced with 4-vinylbenzoate by synthesizing TMPDAVB. The monomer indeed formed 1:2 IC as shown by ^{1}H NMR and the shift in the ester carbonyl of monomer and O−H of β-CD as in the case of TMPTMA and TMPTA.

X-ray Diffraction Analysis of ICs. XRD is one of the physical methods to characterize the crystalline ICs.[10] If the diffraction pattern does not correspond to either of the pure components, i.e., host and guest, formation of a true IC can be inferred.[10,11] All trivinyl monomers are liquid and do not cause X-ray diffraction. Therefore, especially in this case XRD is a very useful technique to study the binding modes of complexation and structure.[11] The XRD patterns of TMPTMA-β-CD and TMPTA-β-CD are isomorphous with the cage-type structure of β-CD (Figure 2a−c). The shift in peak position and emergence of new peaks seen in Figure 2b,c further support the formation of ICs rather than the physical mixture.[3c−h]

Polymerization of ICs. Free radical polymerization of multivinyl monomers leads to cross-linked polymers. But the IC-mediated polymerization of divinyl monomers yields soluble polymers containing pendant unsaturation, as the vinyl group included in the β-CD cavity does not react with growing polymer radicals. Polymerization of all ICs was carried out by free radical solution polymerization in DMF as it dissolved as well as stabilized the IC under polymerization conditions.[12] The polymers obtained were characterized by instrumental methods such as FTIR, NMR, XRD, GPC, and intrinsic viscosity for structure elucidation.

Polymerization of TMPTMA-β-CD (1:2) IC. Poly(TMPTMA) obtained was soluble in $CHCl_3$, THF, DMF, DMSO, and MEK, etc., which are typical solvents for methacrylate polymers. FTIR analysis showed that the isolated polymer was free from β-CD and contained pendant unsaturations.[6,13] ^{1}H NMR analysis showed that only one of the three unsaturated sites in TMPTMA participated in polymerization, as the ratio of the methacrylate groups reacted to methacrylate groups unreacted was 1:2 (Figure 3).

The formation of soluble homopolymer from TMPTMA-β-CD (1:2) IC in DMF was attributed to the stabilization of the IC in DMF.[12] The X-ray diffractogram (Figure 2d) of this polymer after the removal of DMF was crystalline and isomorphous with β-CD and TMPTMA-β-CD IC. The relative peak positions were shifted, which further confirmed the presence of β-CD on poly(TMPTMA).[4] The FTIR spectrum of poly(TMPTMA) prior to the removal of β-CD showed the narrowing of O−H frequency of β-CD and also shift from 3370 to 3338 cm^{-1} and ester carbonyl shift from 1722 to 1729 cm^{-1}. This supports the presence of β-CD in the polymer before decomplexation in water.[12] Thus, inclusion of the methacryloyl group in the β-CD cavity suppresses cyclization, backbiting, and cross-linking during polymerization.[14] The diffractogram of poly(TMPTMA) (Figure 2e) reveals that the neat polymer is amorphous.

The solution properties of the polymer reflect whether it is branched, hyperbranched, dendritic, or linear. The dendritic, hyperbranched, or branched polymers exhibit very low intrinsic viscosity and little dependence on molecular weights since the intermolecular interactions are mostly limited to the surface

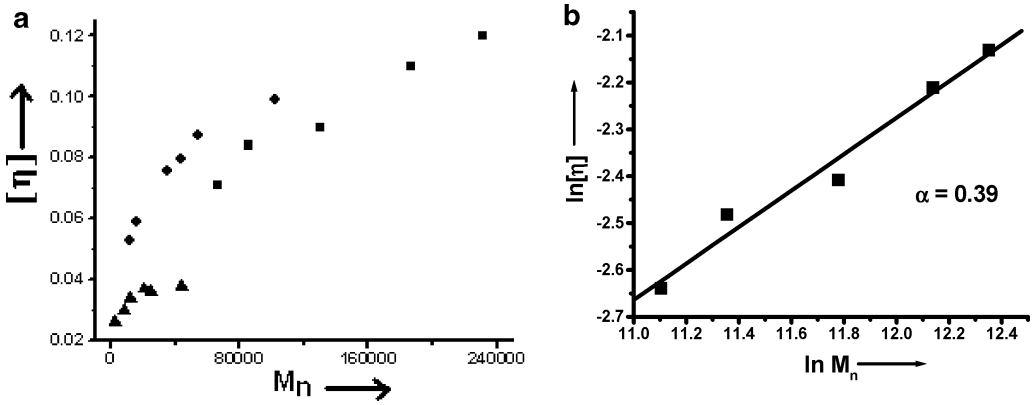


Figure 4. (a) Intrinsic viscosity vs molecular weight plots for (■) poly(TMPTMA), (◆) linear poly(EGDMA), and (▲) hyperbranched poly(EGDMA). (b) Mark−Houwink−Sakurda parameters of poly(TMPTMA).

layers of the spherical macromolecules and do not contribute to intermolecular entanglements.[15a,b] In contrast, linear polymers show a monotonic increase in intrinsic viscosity with molecular weight.[15c] The plot in Figure 4a clearly reveals the dependence of intrinsic viscosity of poly(TMPTMA) on molecular weight as in the case of linear poly(EGDMA). The Mark−Houwink−Sakurda exponent of poly(TMPTMA) is 0.39, while the corresponding values for linear poly(EGDMA)[5] and hyperbranched poly(EGDMA)[15c] are 0.29 and 0.14, respectively. MALLS measurements at 25 °C in THF for poly(TMPTMA) and Zimm plot show $M_w = 6.1 \times 10^5$, which is comparable to M_w obtained by GPC, viz. 2.7×10^5. In contrast, the values differ by an order of magnitude for the branched polymers. For instance, in the case of hyperbranched copolymers of EGDMA Sato et al.[15a] reported $M_w = 1.0 \times 10^5$ by light scattering and 1.9×10^4 by GPC. The value of second virial coefficient, 1.3×10^{-4} mol mL/g^2, for poly(TMPTMA) of M_w 6.1×10^5 is comparable to that for linear poly(EGDMA),[5] viz. 3.5×10^{-4} mol mL/g^2 for the polymer of M_w 2.16×10^5, and is far greater than that for the hyperbranched copolymers of EGDMA,[15a] viz. 7.5×10^{-6} mol mL/g^2 for M_w of 7.68×10^5. All these results confirm linear structure of poly(TMPTMA) obtained by IC-mediated polymerization. The absence of oligomers in the GPC curve also confirms the absence of backbiting during polymerization.

Poly(TMPTMA) containing pendant methacryloyl groups was cast into films and cross-linked by both thermal and UV irradiation. The cross-linked films showed no unsaturation. DSC characterization of polymer in first heating cycle showed T_g at 41 °C, which increased to 57 °C in second cycle. No T_g was observed in subsequent heating cycles due to the formation of densely cross-linked structures.[2d,5]

Polymerization of TMPTA-β-CD (1:1) IC. Since TMPTA formed 1:1 IC, its polymerization was expected to yield a cross-linked product containing unreacted double bonds. Surprisingly, the polymerization of the complex resulted in a soluble polymer containing two double bonds per repeat unit. This could happen if one of the unsaturated sites has a lower reactivity than others. For instance, Nagelsdiek et al.[2e] reported that in the ATRP of allyl methacrylate radical addition to the pendant allyl group does not take place up to 7% conversion. It may be noted here that the probability of a radical attack in a free radical polymerization reaction is greater than in ATRP. Since all unsaturated sites in TMPTA are equally reactive, formation of soluble polymers when conversion exceeds 60% cannot be explained by the above hypothesis. Yet the formation of 1:1 IC indicates that two acryloyl groups can participate in polymerization and hence should lead to a cross-linked product. A more detailed structural analysis of the complex and polymer is therefore warranted at this stage. The ^{1}H NMR spectrum of poly(TMPTA) differs from that of poly(TMPTMA) in that it shows broad signals in the region δ 3.0−4.59 corresponding to six protons (O−CH$_2$−C), as a result of cyclic structure formation through hydrogen bonding between two pendant acryloyl groups (CH···O═C). Also, both free and hydrogen-bonded acryloyl protons were observed in the δ range 5.88−6.41 and 6.98−7.54, respectively (see Supporting Information). The FTIR spectrum of poly(TMPTA) shows pseudorotaxane structure before removal of β-CD and three peaks at 1741, 1732, and 1716 cm^{-1}, indicating the presence of backbone, hydrogen bonded, and free ester carbonyl group in the polymer after removal of β-CD[16] (see Supporting Information). Thus, hydrogen bonding between two pendant acrylate groups of poly(TMPTA) is intact even after polymerization of TMPTA-β-CD (1:1) IC.

Polymerization of TMPDAVB-β-CD (1:2) IC. In order to validate the above hypothesis, one of the acrylate groups in TMPTA was replaced by 4-vinylbenzoate, since it has been shown earlier that this group does not form an IC with β-CD.[5] The monomer TMPDAVB formed 1:2 IC with β-CD and a soluble polymer containing two free acryloyl groups per repeat unit of the polymer. The ^{1}H NMR and FTIR characterization of the poly(TMPDAVB) shows the lack of intramolecular hydrogen bonding between the two acryloyl groups as observed in the case of poly(TMPTA).

At this stage we conclude that both TMPTA and its soluble polymer show the presence of hydrogen bonding between the acryloyl groups, which is absent in the case of soluble polymers of TMPTMA and TMPDAVB. We further believe that the hydrogen bonding between the two acryloyl groups in TMPTA and the lack of it in the case of TMPTMA and TMPDAVB is responsible for the observed differences in the stoichiometry of ICs formed. This requires an independent confirmation of the structure of the complexes. This is best established by molecular modeling.[17]

Molecular Modeling Calculations. To ascertain the composition of the complex, conformational analysis of TMPTMA and TMPTA, and their ICs with β-CD, was undertaken using computational techniques. Conformational analysis was carried out on all the ligands, and various minima on the potential energy were identified using the MCMM method implemented in Schrodinger (Macro model 9.0) program[18] with the MM2* force field. In present study for each molecule, bent and stretched conformations were considered. Both force field and density functional theory, B3LYP/6-31G, calculations indicated that in the case of TMPTA the bent conformation was more

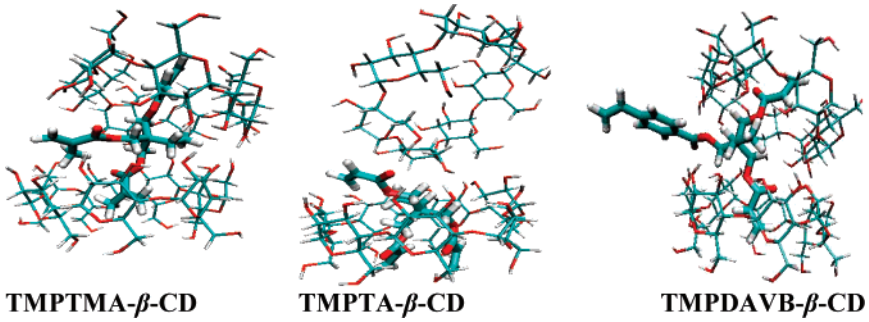


Figure 5. MD simulations of TMPTMA, TMPTA, and TMPDAVB.

stable than linear one by 5−7 kJ/mol, where both conformations formed intramolecular hydrogen bond between C−H···O═C group of two acryloyl groups. The hydrogen bond distances were 3.31 and 3.57 Å and bond angles were 133.7° and 110.2° in bent and stretched conformations, respectively. In the case of TMPTMA, the hydrogen-bonded structure could not be formed. Thus, stretched conformation is more stable than the bent conformation by 8−10 kJ/mol.

Docking, quantum chemical, and molecular dynamics simulations were used to analyze the complexation of the ligands with β-CD. Auto dock 3.0.5,[19] Gaussian 03,[20] and AMBER 8.0[21] programs were used. Rigid docking calculations were performed using Lamarckian Genetic algorithm implemented in AUTODOCK 3.0.5 program by considering the following docking parameters: energy evolutions 1.5×10^6, population size 50, and GA_runs 30. In docking calculations initial geometry of ligand molecules was taken from the optimized geometry obtained at the B3LYP/6-31G level of theory. The lowest energy complex, obtained from the Auto dock calculation, was taken as the initial structure for MD simulations. TIP3P water models were used as solvent with buffer radius of 6.0 Å. The systems considered were minimized with 1000 steps, and molecular dynamics simulations were carried for 10 ns, wherein the first 2 ns was considered for equilibration. The lowest energy conformations of TMPTMA and TMPTA clearly indicated that two β-CDs constituted the IC in the former but only one in the latter case. Thus, the MD simulations clearly accounted for the observed stoichiometry of the ICs. Energies were evaluated at semiempirical and DFT levels of theory, using Gaussian 03 suite of programs, for the lowest energy complex obtained from MD simulations to ascertain the energetics of the sequential addition of β-CDs for TMPTA and TMPTMA. Docking studies and the subsequent binding energies evaluated at the B3LYP/6-31G level of theory revealed that the complexation of the ligand TMPTA with the first β-CD resulted in substantial stabilization of the order of 27−30 kJ/mol, while the addition of a second β-CD did not provide substantial stabilization. TMPTA-β-CD complex is stabilized by an intermolecular hydrogen bond. Carbonyl groups of TMPTA molecule form hydrogen bonds with −OH groups of β-CD. Among the 40 conformations analyzed, 50% showed hydrogen bonding between the carbonyl group of TMPTA and primary −OH groups in β-CD, while only 5% showed hydrogen bonding between the carbonyl group of TMPTA and secondary −OH groups in β-CD. The average bond length and bond angles are 1.77 Å, 169.18° and 1.84 Å, and 177.42° with primary and secondary −OH groups, respectively. The C−H groups of TMPTA attached to electron-withdrawing carbonyl group form hydrogen bonds with β-CD. Of the 40 conformations analyzed 75% showed hydrogen bonding between C−H of the acryloyl group included in β-CD cavity and "O" atom of the primary −OH group. The length and bond angles are 2.67 Å and 143.26°, respectively. In all 85% of the conformations showed hydrogen bonding of one kind or another. On the formation of the inclusion complex, the intramolecular hydrogen bonding in TMPTA molecule has to compete with the formation of intermolecular hydrogen bonds between TMPTA and β-CD, and the degree of intramolecular hydrogen bonding decreases. This intramolecular hydrogen bonding in TMPTA is restored when the β-CD is stripped off from the polymer formed and has been validated experimentally. In the case of TMPTMA the addition of a second β-CD led to substantial stabilization of the order of 46−50 kJ/mol. Thus, the stoichiometry of the complexes is controlled by hydrogen bonding (Figure 5).

In the case of 1:2 IC of both TMPTMA and TMPDAVB, each β-CD cavity contained one methacryloyl or acryloyl moiety. In contrast, in the case of TMPTA, hydrogen bonding between C−H···O═C of two acryloyl groups resulted in the formation of a cyclic structure, which is included within the β-CD cavity. As a result, both acryloyl moieties are included in the same β-CD cavity. FTIR and ^{1}H NMR spectra of the polymer show that the hydrogen bonding between these two acryloyl groups is intact even after polymerization, indicating that the groups have not participated in polymerization due to inclusion in β-CD cavity (see Supporting Information). This explains why a soluble polymer is obtained.

Conclusions

TMPTMA forms 1:2 IC with β-CD, which on polymerization results in the soluble homopolymer containing two free methacryloyl groups per repeat unit. In contrast, TMPTA forms a 1:1 IC with β-CD, and yet the polymerization results in a soluble polymer containing two free acryloyl groups per repeat unit. FTIR as well as ^{1}H NMR analyses of both TMPTA and poly(TMPTA) show the presence of hydrogen bonding in two acryloyl groups. Incorporation of a 4-vinylbenzoate group disrupts the hydrogen bonding between two acryloyl groups in TMPDAVB and restores the formation of 1:2 IC. Molecular modeling analysis shows that hydrogen bonding between the two acryloyl groups results in the formation of a cyclic structure which can now be included in a β-CD cavity. As a result, both the acryloyl groups cannot participate in polymerization although the stoichiometry of the IC is 1:1. The single step methodology described herein can be extended to a wide range of copolymers for applications in microlithography, optical waveguide, and molecular imprinting.[2] Intrachain cross-linking of the copolymers would lead to functional nanoparticles.[2d] Exploiting the concept proposed herein for these applications is a challenge in the development of advanced materials.

Acknowledgment. S.S., R.K., and M.N. thank CSIR, New Delhi, India, for financial support.

Supporting Information Available: NMR, FTIR, XRD, DSC, and molecular modeling calculations of ICs and polymers; complete

refs 20 and 21. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Tomalia, D. A. *Prog. Polym. Sci.* **2005**, *30*, 294−324. (b) Frauenrath, H. *Prog. Polym. Sci.* **2005**, *30*, 325−384.

(2) (a) Liu, J.-H.; Lin, S.-H.; Shih, J.-C. *J. Appl. Polym. Sci.* **2001**, *80*, 328−333. (b) Koo, J.-S.; Smith, P. G. R.; Williams, R. B.; Grossel, M. C.; Whitcombe, M. *J. Chem. Mater.* **2002**, *14*, 5030−5036. (c) Li, Z.; Day, M.; Ding, J.; Faid, K. *Macromolecules* **2005**, *38*, 2620−2625. (d) Mecerreyes, D.; Lee, V.; Hawker, C. J.; Hedrick, J. L.; Wursch, A.; Volksen, W.; Magbitang, T.; Huang, E.; Miller, R. D. *Adv. Mater.* **2001**, *13*, 204−208. (e) Nagelsdiek, R.; Mennicken, M.; Maier, B.; Keul, H.; Hocker, H. *Macromolecules* **2004**, *37*, 8923−8932.

(3) (a) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **2993**, *26*, 5698−5703. (b) Li, J.; Yan, D.; Jiang, X.; Chen, Q. *Polymer* **2002**, *43*, 2625−2629. (c) Harada, A.; Nishiyama, T.; Kawaguchi, Y.; Okada, M.; Kamachi, M. *Macromolecules* **1997**, *30*, 7115−7118. (d) Huh, K. M.; Ooya, T.; Sasaki, S.; Yui, N. *Macromolecules* **2001**, *34*, 2402−2404. (e) Jiao, H.; Goh, S. H.; Valiyaveettil, S. *Macromolecules* **2001**, *34*, 8138−8142. (f) Rusa, C. C.; Bullions, T. A.; Fox, J.; Porbeni, F. E.; Wang, X.; Tonelli, A. E. *Langmuir* **2002**, *18*, 10016−10023. (g) Rusa, C. C.; Luca, C.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 1318−1322. (h) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821−2823.

(4) Chen, L.; Zhu, X.; Yan, D.; Chen, Y.; Chen, Q.; Yao, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 87−90.

(5) Satav, S. S.; Karmalkar, R. N.; Kulkarni, M. G.; Nagaraju, M.; Sastry, G. N. *J. Am. Chem. Soc.* **2006**, *128*, 24, 7752−7753.

(6) Sarvothaman, M. K.; Ritter, H. *Macromol. Rapid Commun.* **2004**, *25*, 1948−1952.

(7) Schneider, H.-J.; Hacket, F.; Rudiger, V. *Chem. Rev.* **1998**, *98*, 1755−1785.

(8) Zhao, T.; Beckham, H. *Macromolecules* **2003**, *36*, 9859−9865.

(9) Jeromin, J.; Ritter, H. *Macromolecules* **1999**, *32*, 5236−5239.

(10) Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 344−362.

(11) Szejtli, J.; Osa, T. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996; Vol. 3 (Cyclodextrins).

(12) Maciejewski, M.; Gwizdowski, A.; Peczak, P.; Pietrzak, A. *J. Macromol. Sci., Chem.* **1979,** *A13*, 87−109.

(13) Storsberg, J.; Ritter, H.; Pielartzik, H.; Groenendaal, L. *Adv. Mater.* **2000**, *12*, 567−569.

(14) Aso, C. *J. Polym. Sci.* **1959**, *39*, 475−486.

(15) (a) Sato, T.; Hashimoto, M.; Seno, M.; Hirano, T. *Eur. Polym. J.* **2004**, *40*, 273−282. (b) Sato, T.; Ihara, H.; Hirano, T.; Seno, M. *Polymer* **2004**, *45*, 7491−7498. (c) Guan, Z. *J. Am. Chem. Soc.* **2002**, *124*, 5616−5617.

(16) Lin, S.-Y.; Chen, K.-S.; Chu, L. R. *Polymer* **1999**, *40*, 2619−2624.

(17) Lipkowitz, K. *Chem. Rev.* **1998**, *98*, 1829−1873.

(18) MacroModel, version 9.0, Schrodinger, LLC, New York, NY, 2005.

(19) Morris, G. M.; Goodsell, D. S.; Halliday, R. S.; Huey, R.; Hart, W. E.; Belew, R. K.; Olson, A. J. *J. Comput. Chem.* **1998**, *19*, 1639.

(20) Frisch, M. J.; et. al. *Gaussian 03, Revision A.1*; Gaussian, Inc.: Wallingford, CT, 2004 (see Supporting Information).

(21) Case, D. A.; et al. *AMBER 8.0*; University of California: San Francisco, CA, 2004 (see Supporting Information).

MA062397I