Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Choi, Soowhan and Ritter, Helmut(2005) 'Formation of Physical Polymeric Gels During Polymerization of Cyclodextrin Complexed *tert*-Butyl Methacrylate in Aqueous Medium', Journal of Macromolecular Science, Part A, 42: 3, 321 — 325
To link to this Article: DOI: 10.1081/MA-200050463
URL: http://dx.doi.org/10.1081/MA-200050463

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 42:321–325, 2005

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1081/MA-200050463

Formation of Physical Polymeric Gels During Polymerization of Cyclodextrin Complexed *tert*-Butyl Methacrylate in Aqueous Medium

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For the first time, radical polymerization of t-butyl methacrylate at 0°C in the presence of methylated β-cyclodextrin in aqueous medium is carried out, leading to the unexpected formation of CD-complexed physical poly(t-BMA) gels.

Keywords cyclodextrin, gel, radical polymerisation, *t*-butyl methacrylate, aqueous medium

Introduction

According to the literature, there are many publications describing the fact that *tert*-butyl methacrylate (*t*-BMA) can be polymerized involving the anionic, radical or emulsion polymerization mechanism. Furthermore, it can be polymerized in bulk or organic solvent (1–8). Recently, Jérôme et al. have reported the radical polymerization of *t*-BMA in water using sodium nitrite as a mediator (9). The emulsion polymerization of vinyl compounds, using cyclodextrins (CDs) (10, 11) in combination with anionic emulsifiers, has been also described (12, 13). Madison and Long investigated the batch polymerization of methacrylic monomers which were complexed by methylated β-CD (14).

We have demonstrated the free radical polymerization of CD-complexed vinyl monomers in water (15–22) and also reported enantioselective polymerization of racemic guest molecules below 0°C, which showed a noticeable enantiodiscriminating influence of CD at low temperatures (23). Recently, the influence of CD on methyl methacrylate (MMA) polymerization at low temperatures on the tacticity of resulting PMMA was detected (24). Regarding our interests, we wish to describe in the present paper the aqueous polymerization of *t*-BMA complexed with methylated β-CD at 0°C.

Received July 2004; Accepted August 2004
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Experimental

Materials and Methods

t-BMA (Fluka) were distilled prior to use. Methylated β-cyclodextrin (CAVASOL, W7M, with an average degree of methylation of 1.8 and of pharmaceutical grade) was purchased from Wacker. IR spectra were run on a Nicolet 5SXB spectrophotometer. GPC analyses were performed with a setup of the PSS company, using tetrahydrofurane (THF) containing 0.1% toluene as eluent at 25°C. The flow rate was 1 mL/min. 100 μL were injected on the column arrangement of PSS: HEMA 10 μ, 40, 100, and 3000 Å porosity. A TSP UV–Vis detector and a Shodex differential refractometer RI 71 were used as detectors. Evaluation was performed using PSS-WinGPC 4.01 software. NMR spectra were recorded with a Bruker AC500 at 20°C. The δ-scale relative to TMS was calibrated by the deuterium signal of the solvent as the internal standard. The glass transition temperature (T_g) of the poly(*t*-BMA) was measured using a Perkin-Elmer Model DSC-7 differential scanning calorimeter in nitrogen atmosphere and 10 mg samples at a scan rate 10 deg/min from 223 K to 473 K. T_g reported as the average of measurements 2–3 using the midpoint method.

General Procedure for the Synthesis of Aqueous t-BMA/m-β-CD Complexes

10 g methylated β-cyclodextrin (CD) was dissolved in 15 mL deionized water. Then, the monomer was added in at least equimolar amounts at room temperature (Table 1). The resulting dispersion was stirred to give a homogenous aqueous *t*-BMA/m-β-CD solution.

General Procedure for the Polymerization of t-BMA/m-β-CD Complexes

To the solution of complex, 0.5 g NaCl was added and flushed with nitrogen and polymerized at 0°C (in an ice bath) using 10 mol-% redox initiator ($K_2S_2O_8/Na_2S_2O_5$) compared to the monomer. After 2 h, the reaction mixture gained high viscosity and the polymerization was terminated by passing air through the reaction mixture. On standing, the terminated reaction mixture formed a physical gel seen in Fig. 1. The gel mixture was warmed in water at 60°C for 1 h, and the polymer precipitated. It was filtered off, washed with 50 ml hot water 2 times, dried in vacuum at 40°C, and analyzed by GPC. Yield: All polymers were obtained in 70% yield.

DSC (2nd heating, −40°C–200°C, 10°C/min): T_g of polymer **1**: 113°C, T_g of polymer **2**: 114°C.

Table 1
Results in the polymerization of *t*-BMA from aqueous methylated β-CD solution at 0°C

Polymer	[*t*-BMA] : [CD] [molar ratio]	Reaction time [h]	M_n [g/mol]	M_w/M_n
1	1 : 1	2	25,000	1.9
2	1 : 1 : 5	2	22,000	1.8
3[a]	1 : 2	> 96	—	—

[a]Polymerization did not happen.

Figure 1. A picture of nearly transparent polymeric physical gels of CD-complexed poly(*t*-BMA).

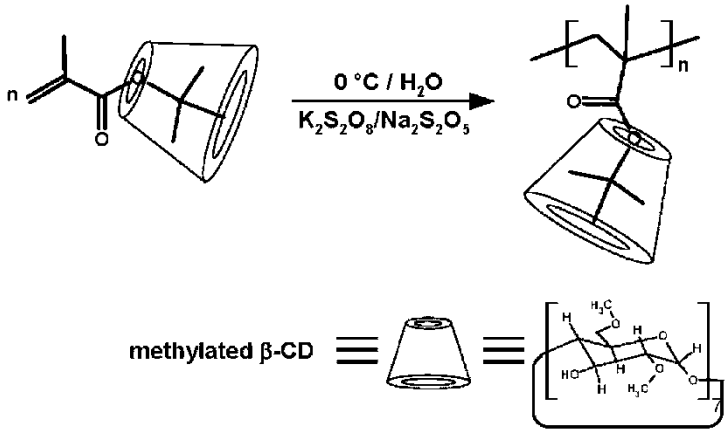
IR (Diamond): $\nu = 2933$ (CH stretching), 1715 (C═O stretching), 1444 (CH aliphatic), 1370 ($(CH_3)_3$), additional bands at: 1147, 1085 cm^{-1}.

^{1}H NMR ($CDCl_3$): $\delta = 2.08-1.70$ ($-CH_2-$ chain), 1.42–1.35 ($-(CH_3)_3$), 1.05–0.90 ($-CH_3$).

^{13}C NMR ($CDCl_3$): $\delta = 177.6$ (CO), 81.2 (quat. carbon), 46.6 ($-CH_2-$), 28.2 (*t*-butyl), 18.9 ($-CH_3$).

Results and Discussion

t-BMA easily complexes with methylated β-CD in water (Sch. 1). In an aqueous solution of methylated β-CD, varying amounts of *t*-BMA were dispersed. After stirring at room temperature, a clear homogenous solution of the complexed *t*-BMA was obtained within a couple of minutes. In this work, radical polymerization of the complexed monomer was carried out at 0°C, salt (2 wt% NaCl) was added to prevent crystallization of water at this temperature (24).



Scheme 1. Polymerization of a *t*-BMA/methylated β-CD complex in water.

It was observed that at room temperature (20°C) the homopolymerization of *t*-BMA takes place readily and the polymer precipitates quantitatively. However, without CD the polymerization occurred very slowly under similar conditions (23). For all the experiments, we applied the redox system potassium persulfate/sodium disulfite as initiator for free radical polymerization. Surprisingly, in contrast to that, the polymerization of CD complexed monomer at 0°C resulted to build a polymeric physical gel. A picture of such polymeric gel is shown in Figure 1. It was found that after starting the polymerization at 0°C in presence of CD, the viscosity of a reaction mixture increased with the reaction time. Finally, after about 2 h the reaction mixture showed very high viscosity leading to physical gel formation.

The polymer was separated from the gelly matter by warming it in water to about 60°C. Uncomplexed poly(*t*-BMA) obtained from the hot solution could be isolated by filtration. The synthesized polymers were characterized by gel permeation chromatography (GPC), ^{1}H NMR spectroscopy and differential scanning calorimeter (DSC). The glass transition temperatures for the polymers were 114°C and 113°C. ^{1}H NMR (0.9–1.1 ppm, $-CH_3$) analyses of polymer products indicated that the cyclodextrin mediated aqueous polymerization resulted in poly(*t*-BMA) similar to that obtained in conventional bulk polymerization. Table 1 illustrates the used molar ratio of host to guest and results of polymerization.

Considering the results, it is obvious that at least an equimolar content of CD in relation to monomer is necessary for a successful physical gel formation during polymerization.

Surprisingly, a polymerization of the complex prepared with a molar ratio of monomer to CD of 1 : 2 does not take place, even after longer times. In this case, obviously the CD-complexed monomers are fully protected by free CD against attack of free radicals. This indicates that beside the complexed *tert*-butyl function, the methacryl group is also included at 0°C in the cavity of a second CD ring.

Conclusions

For the first time, we have demonstrated that the radical polymerization of a CD-complexed monomer in aqueous medium at 0°C leads to formation of polymeric physical gels. These physical gels are stable at room temperature, only at higher temperature an insoluble polymer is obtained. The hydrophilic character of the polymer can be explained by the formation of relative stable polymer-CD complexes.

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