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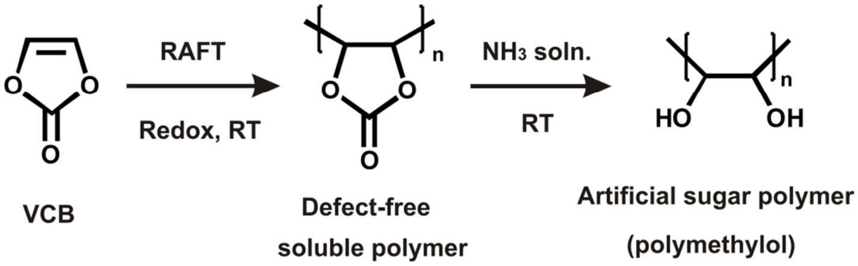

Redox-initiated RAFT polymerization of VCB in microemulsion at RT yields DMF-soluble living polymer, aminolysis of which affords pure polymethylol.

Synthesis of soluble poly(vinylene carbonate) by redox-initiated RAFT process in microemulsion and its aminolysis yielding snow-white polymethylol

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Abstract

Radical polymerization of vinylene carbonate (VCB) above 40 °C yields lightly colored and partially soluble polymers by common procedures. Herein, we describe, a redox-initiated room temperature micro-emulsion process for living polymerization of VCB yielding polymer entirely soluble in DMF, in presence of RAFT agent. Despite first order kinetics the polymerization, molecular weight-time plot exhibited a sudden rise at the beginning and a slow, but linear increment after that, which is typical for the RAFT polymerization in micro-emulsion. This procedure yielded entirely soluble polymers and the gel permeation chromatograms (GPC) implied almost constant polydispersity index (PDI: 1.2) within 20-88 % conversion range. The process was determined to be living as demonstrated by chain extension with styrene yielding diblock copolymer with nearly doubled molecular weight.

Livingness of the process was confirmed by chain extension of the polymer with styrene using photo-iniferter technique. Nearly doubled molecular weight of the resulting polymer within 24 h of irradiation implied formation of vinylene carbonate-styrene block copolymers.

It was demonstrated that VCB homopolymer readily dissolves in ammonia solution (25 %) at room temperature and a snow-white precipitate of the aminolysis product, polymethylol is observed within few minutes. Polymethylol is known as insoluble polymer in common solvents including water due to intermolecular hydrogen bridging. Surprisingly the polymer was determined to dissolve in 80 % of phosphoric acid to give optically clear solutions stable

for over one week at room temperature. ^{1}H NMR spectrum of this polymer in D_3PO_4 indicated pure polymethylol structure.

Key words: Controlled/living polymerization, RAFT, block copolymer, polymer modification, vinylene carbonate.

Introduction

Polymers or oligomers containing five-membered cyclic carbonates have been active area of research due to not only their easy synthesis by action of CO_2 on epoxy compounds but also fast reaction of the carbonate group with nucleophiles such as amines[1-2]. Having vinyl and cyclic carbonate reactive groups, vinyl monomers with cyclic carbonate units are of special interest. A number of cyclic carbonate functional vinyl monomers have been prepared from corresponding epoxy monomers such as glycidylmethacrylate[3], glycidylacrylate[4] glycidyl vinyl ether[5] and 3-butene-1,2-diol[6] by action of carbon dioxide or diethyl carbonate. Polymerization and copolymerization behaviors of those monomers have been investigated in some detail[7-9]. One major application of the polymers with cyclic carbonate groups is based on their rapid reaction with amines yielding hydroxyurethane moieties at room temperature[10]. Cyclic carbonate-amine reaction has been employed for covalent binding of enzymes and proteins in mild conditions[11-13].

Another interesting monomer is vinylene carbonate (VCB) whose polymers and copolymers have similar applications. Despite low polymerization tendency of 1,2-disubstituted ethylenes, this monomer is able to polymerize by radical initiation. Synthesis and radical polymerization of vinylene carbonate was first reported by Newman and Addor[14-15]. Their procedure based on monochlorination of ethylene carbonate and followed dehydrochlorination is still major synthetic route for VCB. Its polymer consisting of five membered cyclic carbonate repeating units, easily hydrolyze to give a water insoluble polymer, polymethylol. Having hydroxyl group in each carbon atom of the repeating unit, this polymer is structurally similar to the achiral sugar so called “formose” which was first described by Alexander Butlerov in 1861[16]. By virtue of extensive intermolecular hydrogen bonding, polymethylol is soluble neither in water nor in common organic solvents, as in the case of cellulose.

The parent polymer, PVCB or its copolymers have similar potential applications in the areas where cyclic carbonate functional polymers are used. Despite being precursor of polymethylol, this polymer might also be of interest as CO_2 source for generating semi rigid foams of some polymers like polyesters. However, the monomer VCB is very expensive due to difficulties in its synthesis and purification. Field and Schaefgen reported that[17]; chlorinated impurities are detrimental in the polymerization, presumably owing to their extensive chain transfer effects. They also reported an improved procedure for purification of VCB and high molecular weight polymers in its polymerization. Dink *et al* studied polymerization of VCB in DMF, DMSO and cyclohexanone at different temperatures[18]. They found that, the polymerization yields partially crosslinked polymers due to side reactions *via* carbonate group at the temperatures above 40 ^oC and colored polymers isolated from the soluble portion were in low molecular weights,. Krebs and Schneider described a radiation initiation method to avoid the side reactions[19]. However the polymerization yields were considerably low.

Also copolymerization of VCB with various vinyl monomers has been reported in few papers. Hayashi and Smets reported the copolymerization of VCB with methyl methacrylate, vinyl chloride, vinyl acetate, vinyl pyrrolidone, styrene, and maleic anhydride[20]. The copolymerization of VCB with other vinyl monomers such as styrene[21] and *N*-vinyl-2-pyrrolidone[22] has been studied by different groups. The literature survey revealed that, polymerization of this monomer is complicated and preparing pure and soluble polymer is still challenging problem. Moreover, there is yet no report on controlled/living polymerization of VCB.

In the present report we describe a redox initiated RAFT process carried out in microemulsion for preparing colorless and completely soluble PVCB. Existence of dithiocarbamate end-groups, thereby livingness of the polymerization was confirmed by chain extension of the resulting polymer with styrene to give block copolymer *via* photoiniferter method. The polymer, PVCB was also subjected to aminolysis. This process gave pure polymethylol and its dissolution in various solvent mixtures has been studied in present work. ^{1}H NMR, FT-IR, GPC, TGA and DSC techniques were employed for structural characterization of the polymers.

Experimental

Materials: Styrene (E. Merck), methyl methacrylate (MMA) (E. Merck) and vinylene carbonate (BOC Sciences) were distilled under diminished pressure prior to use. All the other chemicals; dimethylformamide (DMF) (Aldrich), dimethylsulfoxide (DMSO) (E. Merck), potassium persulfate (KPS) (E. Merck), triethylamine (J. T. Bakers), ammonia (E. Merck), 1-butanol (E. Merck), sodium dodecyl sulfate (SDS) (Aldrich), diethyl amine (J. T. Bakers), carbon disulfide (Aldrich), sodium hydroxide (Aldrich), acetic acid (Aldrich), sodium sulphate (E. Merck) and methanol (J. T. Bakers) were analytical grade chemicals and they were used as purchased.

Characterizations: ^{1}H NMR spectra were taken in DMSO-d_6 solvent, using Agilent VNMRS 500 MHz spectrometer. ^{1}H NMR spectrum of polymethylol was taken in deuteriated orthophosphoric acid which was obtained by mixing 0.5 g P_2O_5 with 1.1 g D_2O.

Gel permeation chromotograms (GPC) were obtained in DMF using Viscotek TDA equipped with Chromatec LCC columns (HR, SE, 4E, 3, and 2), Viscotech 320 pump and refractive index and UV detectors. The measurements were performed at 50 °C at a flow rate of 0.5 mL/min, using polystyrene standard. **FT-IR spectra** were recorded by using Perkin Elmer FT-IR Spectrum One B spectrometer.

Thermo gravimetric analysis (**TGA**) of the PVCB was carried out using Perkin Elmer Diamond TG/DTA under nitrogen atmosphere at a heating rate of 10 °C/min. **Differential Scanning Calorimeter** (DSC) trace of PVCB was taken using Perkin-Elmer Diamond DSC.

Photoreactions were carried out by irradiation at 340 nm using a homemade photo-reactor equipped with 8×12 Watt mercury lamps.

Synthesis of 2-carbomethoxy 2-methyl, ethyl (diethylamino) dithiocarbamate (CAMEDA) (RAFT Agent):

This compound was newly synthesized by a slight modification of the original procedure given in the literature[23]. Thus, in a 250 mL of canonical flask, there was added 8 mL pyridine (0.1 mol), 10.3 mL of diethylamine (0.1 mol) and 15 mL methanol. The flask was immersed in an ice-bath. Meanwhile another 15 mL methanol was mixed with 6.0 mL CS_2(0.1 mol), this mixture was then added drop wise to the first mixture under vigorous stirring at 0 °C. After stirring for 30 min, 10 mL methylmethacrylate (MMA) (0.1 mol) was added to the mixture all at once and stirred for 6 h at room temperature. Finally the mixture was heated at 75 °C for 3 h under reflux condenser. The reaction content was cooled and transferred in a separator funnel.

< Insert Figure 1>

Fifty milliliters of diethylether was added to the mixture and organic phase was separated and washed at least twice with water. The organic phase was dried with anhydrous Na_2SO_4 and chromatographed with a short silica column. The product is obtained as slightly yellow liquid after removal of ether. The yield was 17.7 g (88.4 %). ^{1}H NMR spectrum of the product given in Figure 1 confirms 2-carbomethoxy 2-methyl, ethyl (diethylamino)dithiocarbamate.

Polymerization of VCB in microemulsion using RAFT process at room temperature

Microemulsion process was employed for the polymerization of VCB at room temperature. Thus, in a 100 mL flask, 25 g of distilled water, 0.2 g RAFT agent, 0.3 g KPS, 1.6 g of VCB and 2.75 g SDS were charged and 1.2 g of butanol was added drop wise by pressure equalizing drop structure until the slurry solution becomes clear under the nitrogen flow. After the clear and homogenous solution yielded, 0.3 mL of triethyl amine added and flask was closed to conduct the reaction for 1-8 h while stirring at room temperature. The resulting colorless and clear solution was precipitated in 70 mL methanol and filtered. The product was dissolved in 30 mL acetone and re-precipitated in 100 mL methanol, filtered, washed with diethyl ether and dried under vacuum at room temperature for 24 h. The polymerization yield was assigned based on mass of the white product. Polymerization kinetics of VCB was followed in the same experimental setup by quadruple amounts of each constituent in which aliquots taken at appropriate time intervals and masses of the products isolated by precipitating in methanol were used to construct conversion-time plots of the polymerization.

Preparation of pure polymethylol by aminolysis of PVCB

Hydrolysis of PVCB was carried out by aminolysis with ammonia solution, instead of NaOH solution. For this purpose, 1.72 g of PVCB sample was added to 30 mL ammonia solution (25 %) while stirring. The polymer was completely dissolved within 15 min to give clear solution. Continued stirring for 15-30 min resulted in precipitation of snow-white polymer. The product was filtered, washed with methanol (10 mL), ether (2×10 mL) and dried at 40 ^{o}C for 24 h under vacuum. Dry polymer weighed 0.95 g (82.0 %).

Synthesis of VCB block copolymers with styrene by photo-iniferter technique

PVCB sample (0.3 g) was dissolved in 2.5 mL DMF in a Pyrex tube with a diameter of 2 cm and 15 cm of height. To the reactor there was added 1 mL of styrene under nitrogen flow. The system was closed and irradiated in a photoreactor at 340 nm (8×12 W) for 24 h. The mixture was poured into methanol (25 mL) and the polymer precipitated was dissolved in 10 mL THF and re-precipitated in n-hexane (40 mL).

Results and discussion

Polymerization of VCB by RAFT process at room temperature

To carry out the polymerization at room temperature, first we studied photo-iniferter process using 2-carbomethoxy 2-methyl, ethyl (diethylamino)dithiocarbamate (CAMEDA**)** as chain transfer/ iniferter reagent in bulk conditions. However, irradiation at 256 or 340 nm for 48 h yielded slightly viscous brown solution, from which no polymer was isolated by precipitation in methanol (Table 1).

< Insert Table 1>

Probably this is due to photo-decomposition of the growing ends of the polymer chains by concomitant side reactions of vinylene and carbonate ring as proposed by Ding *et al*[18].

To avoid photo and thermal decompositions, we have also studied polymerization of the monomer by "urea channel complex" methodology[24] using AMPS tetramethylethylenediamine (TEMED) as redox couple. The polymerization did proceed in

15-30 % urea solutions at room temperature and gave voluminous precipitate within 1h. Experiments repeated in various monomer/urea ratios did not helpful to attain a homogenous polymer solution. The resulting white polymers were all soluble in DMF, but molecular weights of the resulting polymers were almost constant (*Mw*: 8800- 9000 Da within 1- 3 h), which is typical for the precipitation polymerization (Table 1).

< Insert Scheme 1>

To overcome those drawbacks, microemulsion with redox initiated RAFT process was developed as an alternative, in which water including surfactant and co-surfactant was used as solvent and the reaction was performed at room temperature (Scheme 1).

This solvent yielded clear solution and the solution remained homogenous throughout the polymerization. The polymerization was demonstrated to be reasonably fast as inferred from noticeable increase in viscosity of the solution within 2 h. No brown color was observed in these conditions and the polymer isolated was completely soluble in DMF, cyclohexanone and NMP.

< Insert Figure 2>

^{1}H NMR spectrum of the polymer (Figure 2) represents one broad singlet at 5.4 ppm. On contrary to the report of Ding group[18], the spectrum does not show ethylenic proton signals of the monomer at 7.6 ppm, implying a defect-free polymer structure.

The polymerization kinetics of VCB in microemulsion was investigated using a molar composition of [monomer]/ [CAMEDA]/ [KPS]/ [TEA]: 100/2/2/2 at room temperature. GPC traces of the kinetic samples taken out at appropriate time intervals show unimodal elution profiles (Figure 3). Sudden rise of the molecular weight (~7000 Da) within first 30 min and gradual increases of the molar mass beyond that. This can be considered typical kinetics of RAFT mediated polymerization in the microemulsion[26]. Mechanism of this behavior has been ascribed to slow diffusion of low mass RAFT fragments[27].

< Insert Figure 3>

The polymerization shows first order ($k = 2.536\times10^{-5}\ s^{-1}$) kinetics with respect the monomer concentration (Figure 4, left), implying a constant radical concentration during the RAFT polymerization. Although the semi-logarithmic plot is fairly linear, it does not pass through the origin implying abnormal fast polymerization in the microemulsion.

< Insert Figure 4>

The kinetic data also revealed a sudden jump in the molar mass and a linear *Mn*-conversion plot (Figure 4, right) beyond that. Interestingly, the polydispersity remains almost constant at 1.2 up to 88 % conversions, which implies good control of the chain growth at [CAMEDA]/ [VCB]: 1/50 molar ratio.

Having cyclic carbonate group, PVCB is expected to yield carbon dioxide upon heating. Thermal behavior of the polymer was simply investigated by TGA. Figure 5 represents a TGA curve with about 10 % of mass loss up to 130 ^{o}C for removal of solvent impurities. A sharp mass loss around 320 ^{o}C (~ 64 %) corresponds to 60.0 % loss in terms of dry polymer. This is higher than the theoretical CO_2 evolution $(44/86)\times100 = 51.1$ %), implying also some concomitant dehydration of the polymer.

< Insert Figure 5>

Gradual mass loss at the temperatures above 320 °C can be ascribed to pyrrolysis of the residual polymer. DSC curve of PVCB (Figure 6, right) represents a small endotherm centered at 110 °C which might correspond to evaporation of the solvent residues. The DSC curve shows a sharp endotherm for the carbon dioxide evolution at 318.5 °C, without melting. Enthalpy of this reaction, 113,5 J/g corresponds to 2.3 kCal/mol. The DSC and TGA traces imply that, PVCB is thermally stable up to 250 °C. and can be considered as potential CO_2 source at elevated temperatures. The inflection of the DSC curve around 190 °C can be ascribed to the glass transition of polymer. Relatively high Tg for the polymer must be stiffness of the cyclic carbonate unit. Therefore, this polymer might be of interest for fabrication of self-foaming materials.

Hydrolysis of PVCB

Hydrolysis of PVCB has been studied by several groups. Since the hydrolysis product, polymethylol is insoluble in common organic solvents its processing is very difficult. Clear solutions of polymethylol formed by alkaline hydrolysis of PVCB with 5 M NaOH at room temperature have been reported to be stable and useful for further reactions[28]. However, the polymer precipitated is no longer soluble. Dink *et al.* studied hydrolysis of PVCB using HCl solution and ethanolamine[18].

< Insert Figure 6>

They observed that, aminolysis with ethanolamine in DMF at 60 °C stops around 40 % of conversion. This was ascribed to the reversibility of the aminolysis reaction. The hydrolysis with HCl solution in acetone was found limited use, due to precipitation of the partially hydrolyzed polymer.

In this work, complete hydrolysis of PVCB was simply achieved by aminolysis with aqueous ammonia solution (25 %) at room temperature. It was observed that, addition of PVCB to the ammonia solution gives a clear solution within 10-15 min and stirring for another 15 min results in precipitation of snow-white polymethylol.

FT-IR spectrum of the aminolysis product (Figure 6b) does not show any trace of carbonyl group vibration band of the parent polymer at 1760 cm^{-1}, which implies a complete hydrolysis. Disappearance of OC-O vibration band of PVCB at 1190 $cm^{-}1$ and new broad band emerged at 3300 cm^{-1} (which is associated with O-H stretching vibration) is additional evidence for the aminolysis. According to simplified scheme of the reaction (Scheme 2**),** the second product is urea rather than ammonium carbonate or carbamate, as inferred from the qualitative carbonate test of the filtered solution.

< Insert Scheme 2>

Polymethylol so obtained was found not soluble in common organic solvents or in their binary mixtures, as reported many times. Even highly polar solvents such as, propylene carbonate, DMF, NMP and their LiCl (10 %) solutions were not able to dissolve this polymer. Insolubility of the polymer has been ascribed to strong intermolecular hydrogen bonding.

Hydrazinium hydroxide (50 % hydrazine solution) is the only solvent known for polymethylol as described in a patent literature[29]. Surprisingly we found that, this polymer is very soluble in phosphoric acid (80-83 %) which is also good solvent for cellulose[30].

< Insert Scheme 3>

Solubility behavior of polymethylol is similar to that of cellulose which is insoluble in water due to intermolecular hydrogen bridging of the hydroxy groups. Protonation of hydroxy groups by action of phosphoric acid precludes the hydrogen bonding between the hydroxy groups. In another words, solubility of the polymer in phosphoric acid (~ 10 %) might be due to suppressing of the intermolecular hydrogen bonding between the hydroxy groups by partial protonation. The polymer can be recovered from the clear solution by precipitation in aqueous Na_2CO_3 solution. Since polymethylol is insoluble in common NMR solvents, its ^1H NMR spectrum was not attainable In order to take ^1H NMR spectrum of this product, in this work we have prepared deuterated phosphoric acid by action of D_2O on P_2O_5 in a tube (Scheme 3).

< Insert Figure 7>

Synthesis of VCB-styrene block copolymers

In order to inspect livingness of the redox initiated RAFT process employed in the polymerization of VCB, the polymer was subjected to chain extension with styrene if dithiocarbamate terminal groups present in the resultant polymer, these will act as initiator/reversible terminator by UV-irradiation at appropriate wavelengths to give block copolymers as reported by Otsu *et al*[31]. In the present work, photoiniferter technique was preferred for the block copolymer formation, to avoid formation homopolymer from the comonomer. This was simply achieved by irradiation of PVCB (*Mn*:9080, *PDI*: 1. 2) in the presence of the comonomer at 340 nm (8×12 W) in DMF solution. GPC traces of the polymer (Figure 8) isolated by precipitation in methanol revealed a molar mass of 17650 Da indicating formation of PVCB-*block*- Polystyrene by photopolymerization.

< Insert Figure 8>

^{1}H NMR spectrum of this polymer (Figure 9) represents presence of both polystyrene and PVCB segments. Appearance aromatic proton signals of polystyrene segments in 6.4-7.3 ppm, in addition to the singlet associated with PVCB proton at 5.3 ppm implies the block copolymer formation. The broad signals at 2.5 and 3.6 ppm represents typical aliphatic signals of polystyrene. Integral ratio of the peak in 6.4-7.3 ppm interval to that of the signal at 5.3 ppm implies a segmental styrene/VCB ratio of 7/12.

< Insert Figure 9>

FT-IR spectrum of this product (Figure 10b) also confirms the block copolymer formation. Strong peak at 1602 cm^{-1} in Figure 8 is well-known ring vibration band of the polystyrene segment. Presence of C=O stretching vibration band of PVCB at 1760 cm^{-1} establishes the copolymer structure.

< Insert Figure 10>

Conclusion

The redox-initiated RAFT polymerization of VCB proceeds with fairly controlled fashion in microemulsion at room temperature and yields completely soluble polymers. On contrary to earlier reports, PVCB is stable in DMF solution, when monomer is pure enough. The simple aminolysis of PVCB proceeds smoothly and results in quantitative hydrolysis to give pure polymethylol, as inferred from ^{1}H NMR spectrum taken in *in situ* generated D_3PO_4 (80 %). It was demonstrated for the first time that, concentrated phosphoric acid is excellent solvent for polymethylol. Being polymeric analogue of the reduced sugars, this polymer might be of interest in biomedical applications. Presence of reactive dithiocarbamate end groups on PVCB was confirmed by photoinitiated chain extension with styrene at 340 nm of wavelength in

DMF solution. ^{1}H NMR and FT-IR spectra of the polymer establish block copolymer structures.

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Legends

Figure 1. ^{1}H NMR spectrum of the RAFT agent in $CDCl_3$.

Figure 2. ^{1}H NMR spectrum of VCB (a) and its polymer (PVCB) (b) in DMSO-d6.

Figure 3. GPC traces of PVCB samples in DMF showing mass increase with the polymerization time.

Figure 4. First order kinetics plot (left) and *Mn* and PDI of the polymers as a function of conversion (right) for redox initiated RAFT polymerization of VCB at room temperature.

Figure 5. TGA (left) and DSC (right) traces of PVCB prepared by RAFT process at room temperature (under nitrogen at a heating rate of 10 ^{o}C/min.)

Figure 6. FT-IR spectrum of PVCB prepared by modified radicalic microemulsion process (A), and its aminolysis product, polymethylol (B).

Figure 7. ^{1}H NMR spectrum of polymethylol obtained by room-temperature aminolysis of PVCB (taken in D_3PO_4).

Figure 8. Gel permeation chomatogram of the copolymer obtained by chain extension of PVCB with styrene by photoiniferter method.

Figure 9. ^{1}H NMR spectra of PVCB (a) and its block copolymer obtained by chain extension with styrene(b) in DMSO-d_6.

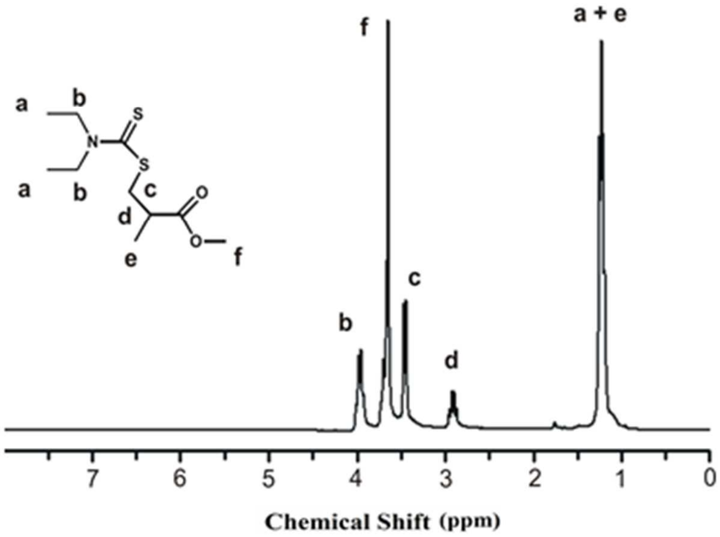
Figure 10. FT-IR spectra of PVCB prepolymer (a) and the polymer obtained by its chain extension with styrene by photoiniferter process (b).

Scheme 1. Polymerization of VCB by redox initiated RAFT process and followed aminolysis yielding polymethylol at room temperature.

Scheme 2. Aminolysis of PVCB yielding pure polymethylol at room temperature.

Scheme 3. Preparation of deuteriated ortho-phosphoric acid.

Table 1. Various room temperature processes studied for the polymerization of VCB.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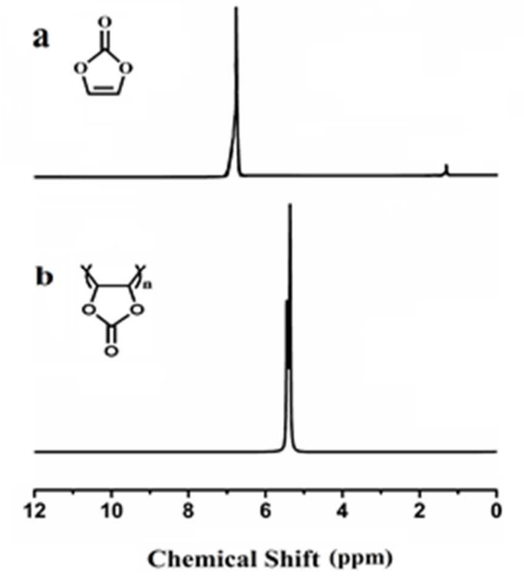
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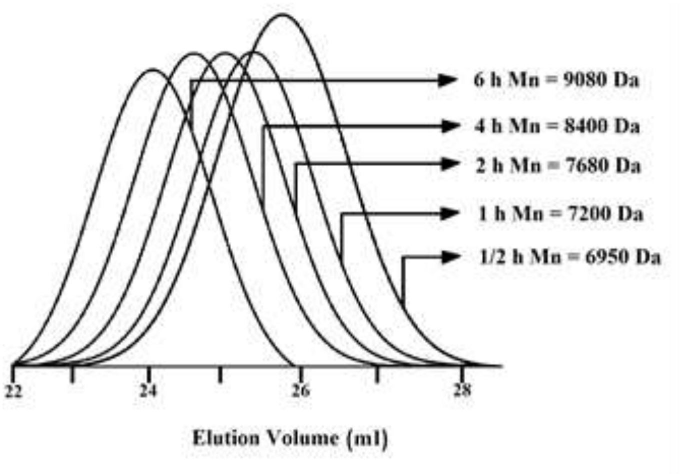
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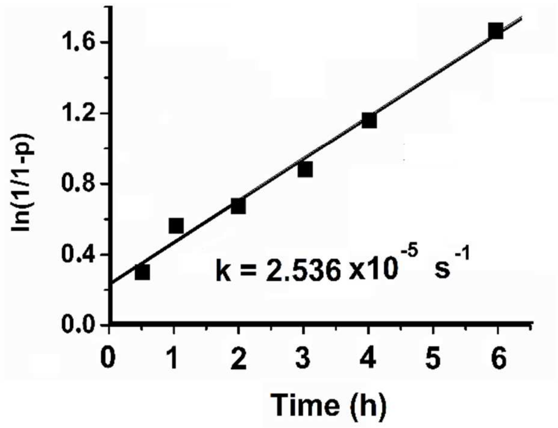
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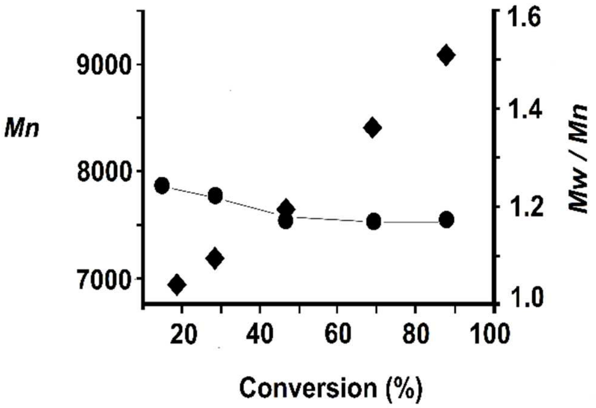
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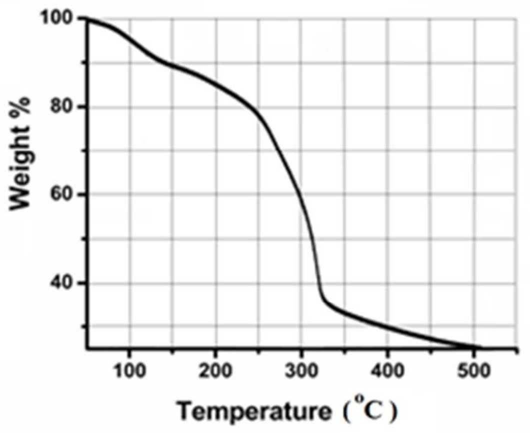
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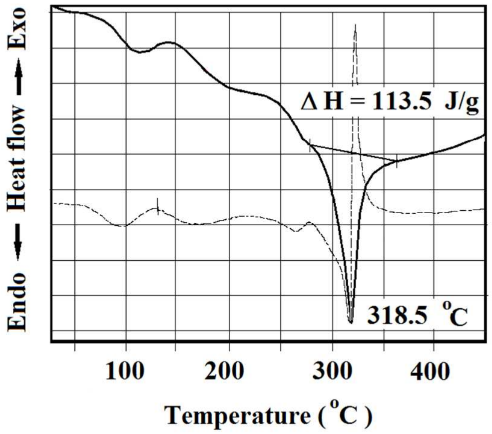
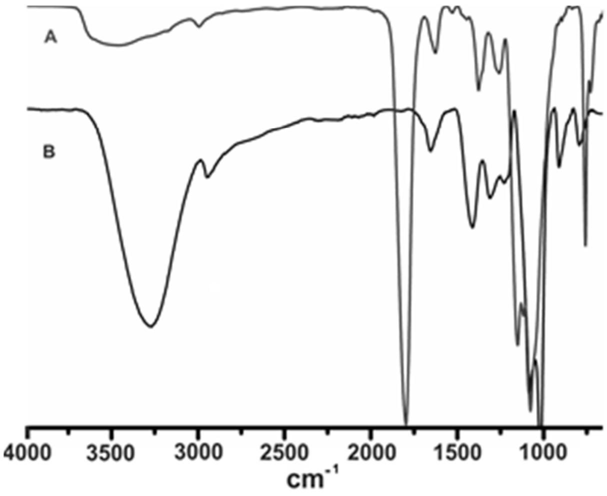
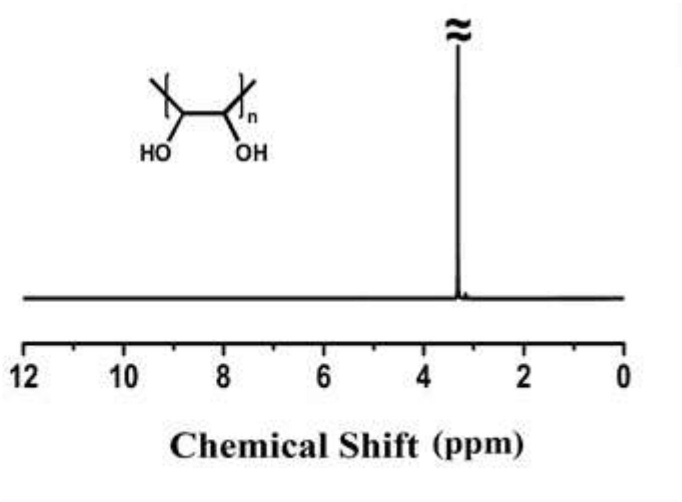
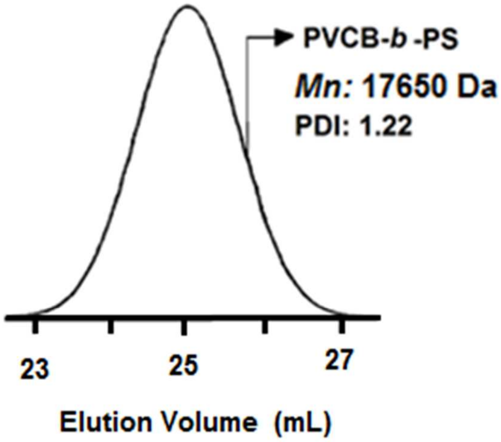
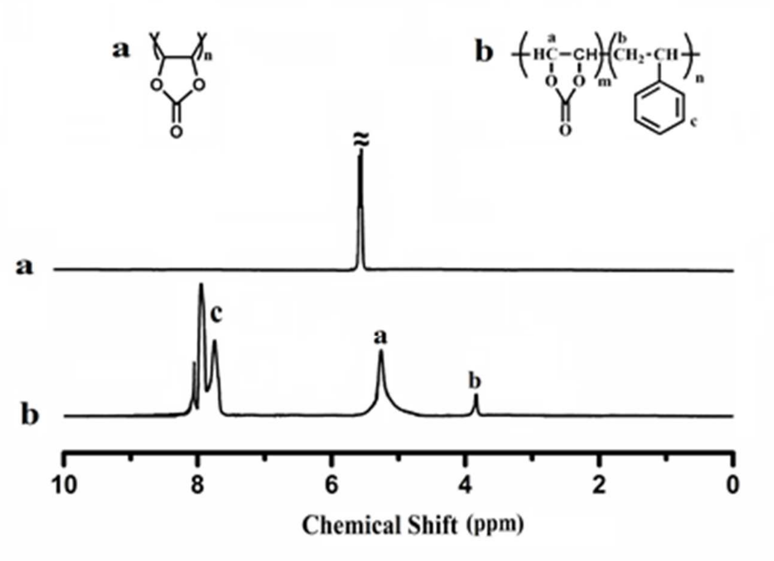
500
Temperature (°C)

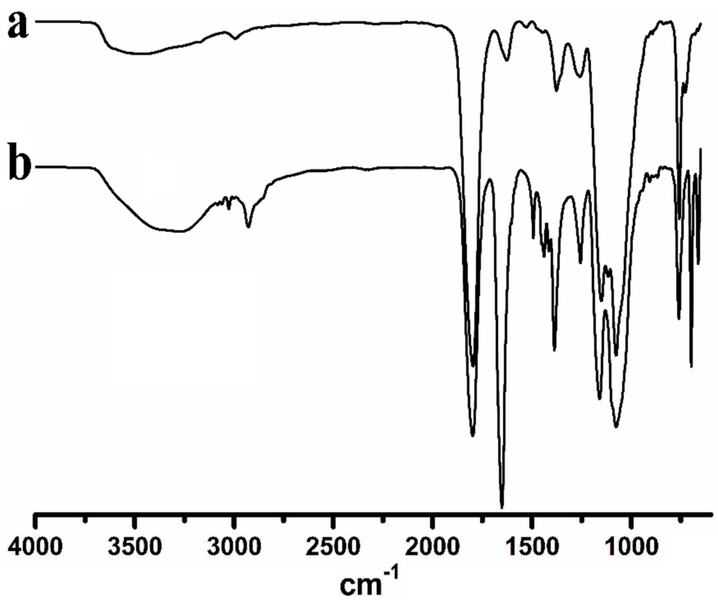

Endo ⟵ Heat flow ⟶ Exo
ΔH = 113.5 J/g
318.5 °C
100
200
300
400
Temperature (°C)

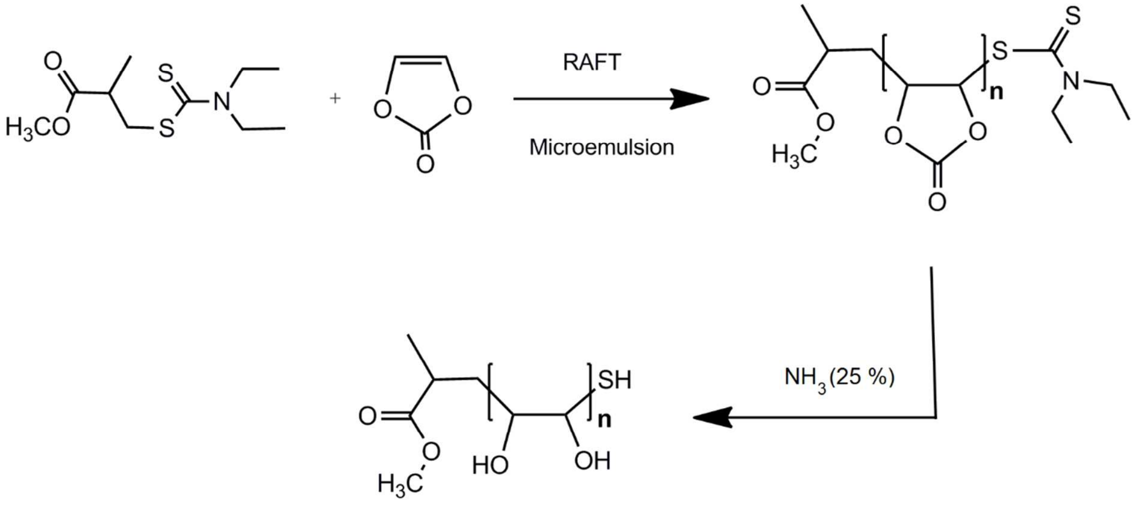

A
B
4000
3500
3000
2500
2000
1500
1000
cm^{-1}

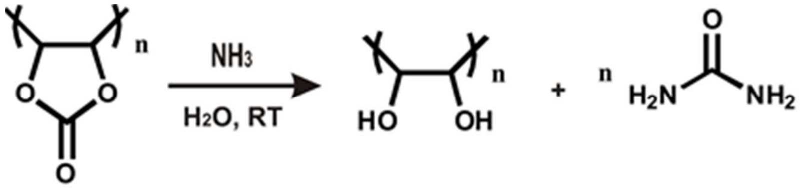

HO
OH
n
12
10
8
6
4
2
0
Chemical Shift (ppm)


PVCB-*b* -PS
Mn: 17650 Da
PDI: 1.22
23
25
27
Elution Volume (mL)


a
b
a
b
c
a
b
10
8
6
4
2
0
Chemical Shift (ppm)


a
b
4000
3500
3000
2500
2000
1500
1000
cm^{-1}


H$_3$CO
O
S
S
N
+
O
O
O
RAFT
Microemulsion
O
H$_3$C
O
S
S
N
n
O
O
O
NH$_3$ (25 %)
O
O
H$_3$C
SH
n
HO
OH


n
NH3
H2O, RT
HO
OH
n
+
n
O
H2N
NH2
O
O
O

$$3\ D_2O\ +\ P_2O_5 \longrightarrow 2\ D_3PO_4$$

Polymerization method	*Conditions*	*Initiator*	*Time*	*Yield (%)*	*Mv* [a]
Photo-iniferter	(8×12 W) Bulk, RT	CAMEDA (1/50)	48 h	No polymer	-
	Urea soln (20 %) RT, 15 % VCB	AMPS-TEMED (Redox)	1 h	98.8	8800
Urea Channel	Urea soln (20 %) RT, 15 % VCB	AMPS-TEMED[b] (Redox)	3 h	100	9000
RAFT	CAMEDA (1/50) In microemulsion RT, 15 % VCB	AMPS-TEA[b] (Redox)	1.5 h	21.5	6500

(a): The weight average molecular weights estimated from viscosities using Mark-Houwink parameters[25]. (b): [AMPS]/ [VCB] ratio is 1/50.