Carbohydrate Polymers 83 (2011) 74–80

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Synthesis and characterization of thermo-sensitive graft copolymer of carboxymethyl guar and poly(*N*-isopropylacrylamide)

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ARTICLE INFO

Article history:
Received 9 June 2010
Received in revised form 8 July 2010
Accepted 10 July 2010
Available online 16 July 2010

Keywords:
Carboxymethyl guar
Poly(*N*-isopropylacrylamide)
Thermo-sensitivity and graft copolymer

ABSTRACT

Thermo-responsive graft copolymers of carboxymethyl guar [CMG] and semitelechelic poly(*N*-isopropylacrylamide) [PNIPAm] were synthesized by coupling reaction between them using a water-soluble coupling agent namely, 1-(3-(dimethylamino) propyl)-3-ethyl carbodiimide hydrochloride [EDC]. The incorporation of PNIPAm into CMG was confirmed by FT-IR and NMR spectroscopy. The graft copolymers, CMG-g-PNIPAm showed enhanced viscosity as compared to the unmodified CMG in the semi-dilute regime. Due to the presence of a LCST side chains [PNIPAm], the graft copolymers exhibited thermo-responsive nature with respect to temperature which was investigated using pyrene fluorescence probe studies. Although the thermo-responsive property was observed, the thermo-thickening behavior was not seen in these polymers. The graft copolymers in the semi-dilute regime ($C_p \approx 10$–20 g/L) showed viscoelastic properties and the relaxation time, τ, could be obtained from the crossover of frequency (ω_c) of storage modulus (G') and loss modulus (G'') in the oscillatory experiments. The activation energy 'E_a' of associations was investigated using the time temperature superpsition (TTS). These thermo-responsive polymers along with the biodegradability of CMG can have potential application as industrial thickening agent.

1. Introduction

Guar gum (GG) is a naturally occurring non-ionic, hydrophilic polygalactomannan polysaccharide derived from the seed of guar gum plant (Whistler, 1959). The chemical structure of GG consists of anhydro-D-mannose units linked to each other by β(1, 4) linkage to form the backbone chain and anhydrogalactose units are connected to alternate mannose units by β(1, 6) linkage. Carboxymethyl guar is a chemically modified GG (using carboxymethylation), which exhibits high water solubility and good clarity.

In the past, polysaccharides such as carboxymethyl cellulose, chitosan, dextran and starch have been chemically modified with synthetic polymers to obtain products with synergistic properties. One of the common methods is to graft copolymerize variety of synthetic monomers onto polysaccharide backbone via free radical polymerisation (Bahamdan, 2005). However, in this methodology there is no control on the grafted pendant chain and sometimes one can end up getting crosslinked polymers due to the coupling of propagating polymer chain ends. The other strategy followed is the grafting of end-functionalized polymers to functional groups of polysaccharides, using coupling reactions. For example, graft copolymers with various lengths of grafts were obtained using coupling reaction between carboxymethyl dextran and end functionalized poly(NIPA-co-DMA) in the presence of a water-soluble coupling agent, carbodiimide (Esquenet & Buhler, 2001).

In the recent past, many studies have been devoted to hydrophobically modified polysaccharides. For example, hydrophobically modified chitosan polymers have been reported in the literature (Bhattarai et al., 2008; Kjoniksen, Iversen, Nystrom, Nakken, & Palmgren, 1998; Thatte, 2004; Yan-Yan et al., 2006). Bokias, Mylonas, Staikos, Bumbu & Vasile (2001) have reported thermo-responsive graft copolymers of carboxymethyl cellulose (CMC). An interpenetrating networks (IPNs) based on guar gum and poly(*N*-isopropylacrylamide) PNIPAm, with a major focus on swelling kinetics has been reported (Li, Wu & Liu, 2008). Recently, Zhang et al. (2009) have reported on the synthesis and characterization of thermo-sensitive graft copolymer of poly(*N*-isopropylacrylamide) and carboxymethyl chitosan. Similarly, Shi and Zhang (2007) studied the grafting of poly(*N*-isopropylacrylamide) onto carboxymethyl hydroxypropyl guar (CMHPG). However, it was intriguing to note from their study that they did not observe the formation of hydrogel in their system but obtained thermo-sensitive polymer solutions. Furthermore, the polymer solutions did not exhibit thermo-thickening behavior as observed by Bokias et al. (2001) in a similar thermo-associating polymer system. Kang Moo, Junko, Toor and Nobuhiko (2000) reported on the synthesis and characterization of carboxymethyl dextran and poly(*N*-isopropylacrylamide-*co*-*N*,*N*-dimethylacrylamide).

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doi:10.1016/j.carbpol.2010.07.023

In most of the above studies, when an LCST polymer is covalently linked as a pendant chain to a water-soluble polysaccharide backbone, the overall polymers exhibit a thermo-responsive property in aqueous medium and the optical transmission with respect to increase in temperature showed discontinuous transition at LCST of pendant chains (Jeong & Gutowska, 2002). Therefore, it is not still very clear from the literature about the pre-requisites in a thermo-associating system to be able to show the thermo-thickening behaviour.

In the present paper, we report on the synthesis and solution properties of graft copolymers based on carboxymethyl guar (CMG) backbone bearing thermo-sensitive PNIPAm side chains, CMG-g-PNIPAm. The grafting was performed by coupling reaction between amino-terminated PNIPAm and CMG using water-soluble EDC as a coupling agent. The structural characteristics of graft copolymers were performed using FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The solution behavior of the polymers was studied using fluorescence spectroscopy and rheometry. Grafting of PNIPAm side chains onto hydrophilic CMG backbone is expected to provide CMG with new thermo-sensitive properties in solution. The viscoelastic properties at moderate concentration were explained in terms of storage modulus (G') and loss modulus (G''). The time temperature superposition (TTS) was performed to estimate the activation energy for the associations.

2. Experimental

2.1. Materials

Carboxymethyl guar (CMG) was a commercial product and was kindly provided by Hindustan Gums, Haryana, India. *N*-isopropylacrylamide (NIPAm) and 2-amino ethane thiol hydrochloride (AET·HCl) were purchased from Aldrich Chemical Company, USA. The coupling agent, 1-(3-(dimethylamino) propyl)-3-ethyl carbodiimide hydrochloride (EDC) was obtained from Fluka, USA and was used as such. Potassium persulphate (KPS) along with other solvents were of analytical grade and were obtained from S.D Fine Chemicals, India. The chemicals were used as received. Water was purified using a Millipore laboratory unit (Q-Millipore, 18.2 MΩ).

2.2. Purification of CMG

The commercial CMG obtained from an industry was purified using the following procedure.

10 g of CMG was taken in a 1 L conical flask and 500 ml acetone was added. The entire mass was stirred with a magnetic needle on a magnetic stirrer for 12 h at room temperature. Then it was filtered and dried. The dried CMG was dissolved in 1 L distilled/deionised water and centrifuged at 10,000 rpm for 40 min. The supernatant liquid was dialyzed against water using a dialysis membrane with MWCO of 12 kDa. The dialysis was carried out for 24 h by frequently changing the external water. The dialyzed solution was then freeze-dried to obtain white cotton like material. The purified CMG was used for all the experiments.

The molecular weight (MW) of CMG was determined by measuring its intrinsic viscosity, [η] in water at 25 °C using ubbelhode capillary viscometer. The MW was found to be 860 kg mol^{-1}. The carboxymethyl content was 9.28 mol% as determined by acid–base titration using a pH meter.

2.3. Synthesis of amino-terminated PNIPAm [PNIPAm-NH_2]

Amino-terminated PNIPAm was prepared by free radical polymerization of NIPAm monomer in aqueous solution by using a redox initiator pair KPS/AET·HCl (Durand & Hourdet, 1999). The polymerization was carried out in a three necked flask equipped with a reflux condenser, a magnetic stirrer and a nitrogen inlet. The monomer (1.24 mol/L) was dissolved in water and the solution was deaerated with nitrogen gas. The temperature was maintained at 30 °C using a water circulating system. The initiator, KPS (0.025 mol/L) and the chain transfer agent, AET·HCl (0.025 mol/L) were separately dissolved in water (10 ml) and added to the monomer solution. The reaction was continued for 18 h and the polymer was recovered by dialyzing against water using a membrane (cut off 3.5 kDa). Finally the dialyzed solution was freeze-dried. The product was redissolved in minimum amount of methanol and the hydrochloride ions were neutralized using NaOH and solution was concentrated to remove traces of methanol. The polymer was precipitated in excess of diethyl ether, decanted and vacuum dried. To this, chloroform was added and the solution was filtered to remove NaCl, and NaOH. The polymer was concentrated and vacuum dried.

Table 1
Stoichiometry of reactants for the synthesis of CMG-g-PNIPAm polymers.

Samples	CMG (g)	PNIPAm (g)	EDC (g)
CMG-g-PNIPAm10-5 (CMP10-5)	10	0.925	0.137
CMG-g-PNIPAm10-10 (CMP10-10)	10	1.85	0.274
CMG-g-PNIPAm10-27 (CMP10-27)	10	5	0.740

Code: For example, CMP10-5 corresponds to a copolymer containing 5 mol% of PNIPAm with a MW of PNIPAm 10.5 kg/mol.

2.4. Synthesis of graft copolymers

The CMG-g-PNIPAm copolymers were prepared by a coupling reaction between CMG and PNIPAm-NH_2 using water-soluble EDC as a coupling agent. Totally, three graft copolymers were prepared with different contents of PNIPAm-NH_2 molecular weight 10,500. Stoichiometry of the reactants and the nomenclature of the samples are shown in Table 1.

In a typical synthetic procedure of the graft copolymer containing 9.28 mol% carboxymethylation, 10 g of CMG and 1.85 g PNIPAm-NH_2 were dissolved separately in 980 ml and 20 ml water respectively under stirring for 15 h. The two solutions were then mixed at room temperature and pH was adjusted to 8.0 by adding 1 M NaOH solution. To the above mixture, 0.274 g of EDC dissolved in 5 ml of water was added and stirred for 8 h at room temperature. Then the mixture was dialyzed against distilled water and further extracted with chloroform for 6–8 h to remove unreacted PNIPAm. Finally, the product was freeze-dried to obtain in the pure form.

2.5. Characterization of amino-terminated PNIPAm

The molecular weight of PNIPAm-NH_2 were determined by both end group analysis method and gel permeation chromatography (GPC).

The average molecular weight and polydispersity of PNIPAm-NH_2 were measured by size exclusion chromatography (SEC) using polystyrene gel columns 1_60 cm 100 Å and 1_60 100 Å from PSS GmbH standards. The solvent, chloroform was used as an eluent at a flow rate of 1 ml min^{-1}.

The molecular weight by end group analysis was performed by pH titration where in, the PNIPAm-NH_2 was titrated with standardized 0.01N HCl using a pH meter. This uses an electrode whose potential depends on the amount of H^+ ion present in the solution. At the endpoint, there will be a sudden change in the measured pH to calculate the moles of acid took to neutralize the PNIPAm base (NH_2). From this data, the MW of PNIPAm-NH_2 could be calculated.

2.6. FT-IR spectroscopy

The FT-IR spectra of all the samples were recorded from a FT-IR spectrum-1 Perkin Elmer Spectrometer, UK in a diffused reflectance mode. The samples were mulled with KBr and the frequency range was from 400 to 4000 cm^{-1}.

2.7. ^1H NMR spectroscopy

The ^1H NMR spectra of CMG, PNIPAm-NH_2 and graft copolymers were recorded in D_2O using Bruker DRX-500 spectrometer operating at a proton frequency of 500.13 MHz.

2.8. Fluorescence spectroscopy

Steady state fluorescence was recorded on a Perkin Elmer LS55 Luminescence spectrometer equipped with a circulating water bath to control the temperature of the measuring cell. Pyrene solution in acetone (1×10^{-3}M) was used as an external probe in a final concentration of 6×10^{-7}M. The excitation wavelength was 339 nm. The change in the intensity ratio (I_1/I_3) of the first and the third vibronic bands at 373 nm and 384 nm for I_1 and I_3 respectively in the emission spectra were used to detect the hydrophobic microdomains.

2.9. Viscometry

Reduced viscosity measurements for PNIPAm-NH_2 and copolymers were carried out using an automated capillary viscometer system, SCHOTT-GERATE AVS-470, viscometer, Germany with a capillary diameter of 0.64 mm and a temperature controller circulating bath with an accuracy of ±0.01 °C. The reduced viscosity was calculated as a ratio of $(t–t_o)/t_oC_p$, where 't_o' and't' are the flow times of solvent and the polymer solution of concentration 'C_p'. The intrinsic viscosity, [η] was determined from the extrapolation of the reduced viscosity curve to zero concentration.

2.10. Rheometry

Steady state viscosity measurements of polymer solutions were performed on an Anton Paar MCR-301, controlled stress rheometer by using a cone-and-plate geometry (diameter = 50 mm, angle = 1°) for highly viscous gel samples. For low viscosity samples, cuvette (coaxial cylinder) geometry was used to measure viscosity.

Dynamic experiments were performed at 15–30 °C with an interval of 5 °C. Initially, the sample was subjected to a strain sweep at a fixed frequency of 1 Hz to determine the linear regime. Then the frequency sweep experiments were performed in the linear regime to determine storage (G') and loss (G'') moduli in the frequency range of 0.01–100 Hz (rad/s).

2.11. Sample preparations

All the solutions were prepared using pure deionized water. Very gentle stirring was employed to get homogeneity of the sample before taking them for experiments.

3. Results and discussion

3.1. Synthesis of PNIPAm-NH_2, graft copolymers and their characterization

Semitelechelic, PNIPAm-NH_2 homopolymers containing reactive group at one end of the polymer chain were prepared by free radical polymerization in aqueous solution using 2-aminoethane thiol hydrochloride as a chain transfer agent. In order to avoid the phase separation of PNIPAm during the polymerization, the reaction temperature was maintained at 30 °C, which is below the LCST of PNIPAm. This ensured the homogenous polymerization of the NIPAm monomer. We show in Table 2 the results of molecular weights obtained by both GPC and end group analysis using pH titration methods.

Table 2
The molecular weight and PDI for PNIPAm-NH_2.

Sample	M_n[a]	M_w[b]	P.D.I.[a]	M_n[b]
PNIPAm10	1.12×10^4	1.90×10^4	1.69	1.05×10^4

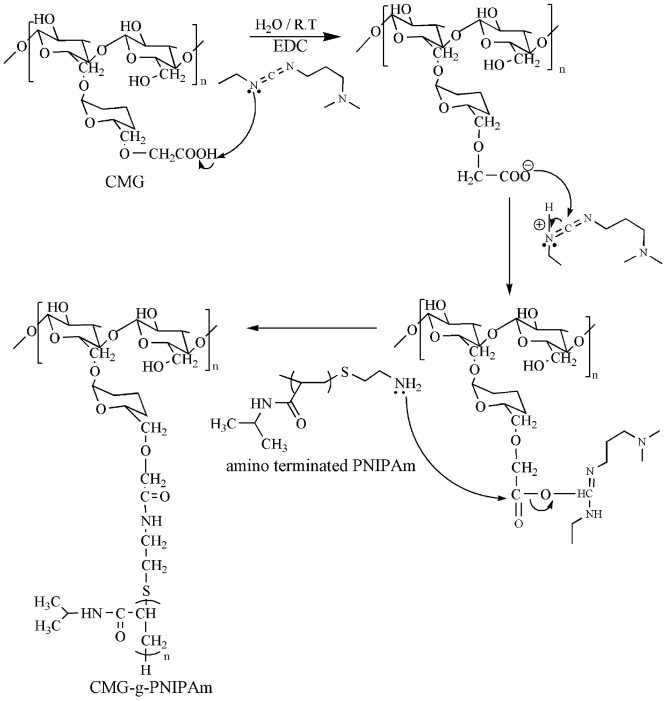
[a] Gel permeation chromatography (in $CHCl_3$).
[b] pH titration method.

It can be readily seen from the table that the M_n obtained by GPC matches reasonably well with the pH titration method. The polydispersity index shows that the distribution of molecular weights is not too broad. Graft copolymers, CMG-g-PNIPAm, were obtained from coupling reaction between CMG and PNIPAm-NH_2 in the presence of a water-soluble carbodiimide as a coupling agent. The pathway for coupling reaction is shown in Scheme 1. Totally, three different graft copolymers were prepared with different contents of PNIPAm-NH_2 of molecular weight 10,500 g/mol.

3.2. FT-IR spectroscopy

We show in Fig. 1, the IR spectra of CMG, PNIPAm-NH_2 and the graft copolymer CMP10-10.

Compared to the homopolymers, CMG and PNIPAm-NH_2, the graft copolymer shows characteristic peaks around 3500–3200 cm^{-1} which can be attributed to the stretching of –OH from CMG and –NH from PNIPAm chains. Further, the bands at 1652 cm^{-1} and 1541 cm^{-1} corresponds to the C=O stretching of amide I and –NH stretching of the amide II of PNIPAm. These results clearly indicate the incorporation of PNIPAm into CMG.



Scheme 1. The mechanism of coupling reaction of PNIPAm-NH_2 to CMG.

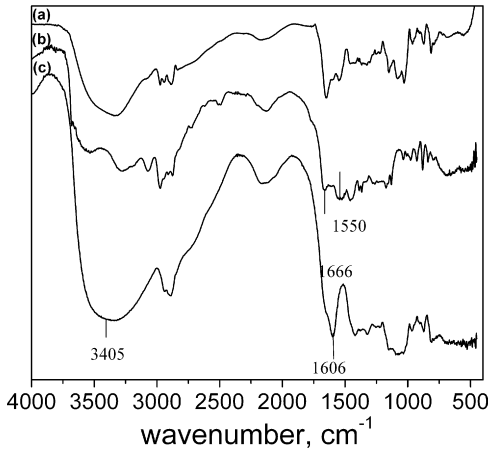


Fig. 1. FT-IR spectra for (a) CMP10-10, (b) PNIPAm-NH_2 and (c) CMG.

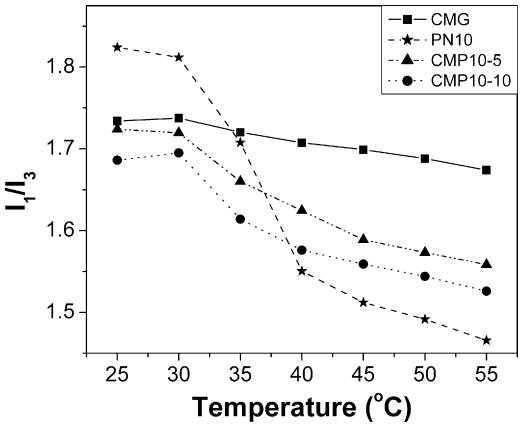


Fig. 3. Variations of the ratio of I_1/I_3 as a function of temperature for CMG, PNIPAm-NH_2, CMP10-5 and CMP10-10. The polymer concentration is 2 mg/ml.

3.3. ^1H NMR spectroscopy

In order to further confirm the presence of PNIPAm in the graft copolymer, we performed ^1H NMR spectroscopy. Fig. 2 shows the ^1H NMR spectra of CMG, PNIPAm-NH_2 and CMP10-10 graft copolymer.

It can be readily seen from the figure that, the graft copolymer, CMG-g-PNIPAm showed the characteristic peaks of both CMG and PNIPAm protons. The $-CH_3$ proton of PNIPAm-NH_2 and the graft copolymer appeared at 1.12 ppm which is completely absent in the homopolymer of CMG. Similarly, the –OH proton peak of CMG and CMG-g-PNIPAm appeared in the region of 3.5–4.5 ppm. The observation of characteristic proton peaks arising from both PNIPAm and CMG in the graft copolymer confirmed the structure of the graft copolymer.

3.4. Fluorescence spectroscopy

Fluorescence spectroscopy has been extensively used to study the hydrophobic micro-environment of amphiphilic polymers in aqueous media with pyrene as a probe. Two important properties of pyrene, a change in the intensity ratio of the first over third vibronic peak (I_1/I_3) in emission spectra and a (0, 0) band shift in excitation spectra upon the formation of hydrophobic micro-environment in aqueous media, are utilized to study the aggregation behavior of micelles.

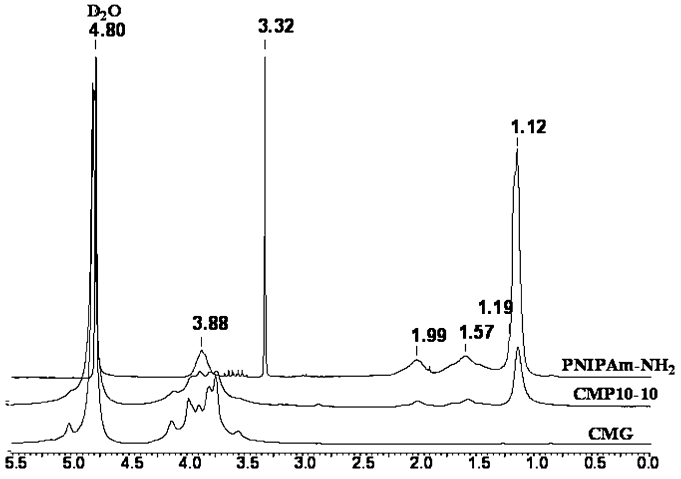


Fig. 2. ^1H NMR spectra of (i) CMG, (ii) PNIPAm-NH_2 and (iii) CMP10-10.

Fig. 3 shows the change in the intensity ratio (I_1/I_3) of pyrene excitation spectra as a function of temperature for CMG, PNIPAm-NH_2 and two copolymers CMP10-5, CMP10-10. For the homopolymer PNIPAm, there was no significant change in the intensity ratio at low temperature region (below LCST). However, a sharp decrease in the intensity ratio was observed at temperature close to the LCST of the polymer (~32–33 °C), revealing the formation of hydrophobic micro-environment at this temperature. The high values of intensity ratio (I_1/I_3) indicate an aqueous polar environment whereas, lower values indicate the low polarity micro-environment where pyrene molecules can be solubilized (Shalaby, McCormick & Butler, 1991).

In the case of CMG homopolymer, there was no rapid decrease in the intensity ratio (I_1/I_3) at any temperature in the whole temperature range studied, indicating that there are no hydrophobic domains formed in the solution. Nevertheless, a small continuous decrease of the intensity ratio (I_1/I_3) with temperature was observed which could be due to the behavior of pure pyrene solutions. The graft copolymers, on the other hand showed a considerable decrease in the intensity ratio (I_1/I_3) above the LCST of the grafted PNIPAm chains indicating the formation of hydrophobic microdomains. It can be attributed to the fact that, above the LCST of the grafted chain in the copolymer, a polymer-rich phase can form from the collapsed and precipitated PNIPAm chains, followed by a solubilization of pyrene in polymer-rich hydrophobic micro-environment. It can be noted that, we observed a weaker hydrophobic microdomains in graft copolymers as compared to the homopolymer, PNIPAm above the LCST.

These results clearly indicate the thermo-responsive nature of the CMG-g-PNIPAm copolymers. However, it is intriguing to note that, although we observed a thermo-responsive behavior in these graft copolymers, the thermo-thickening property was not seen as reported earlier in some related systems such as carboxymethylcellulose-g-PNIPAm (Bokias et al., 2001) and chitosan-g-PEG (Zhang et al., 2009). We do not know the reason at this moment but realize that there could be many factors such as hydrophilicity/solubility of the backbone chain, the frequency and molecular weight of the grafted chain which can contribute to the observation of thermo-thickening behavior.

We also determined the critical aggregation concentration (cac) by recording the ratio of intensity (I_1/I_3) against the polymer concentration 'C_p' (mg/ml). We show in Fig. 4 the semi-log plot of intensity ratio (I_1/I_3) versus the concentration, 'C_p'.

The curve with 3 tangents and the cross over point obtained by using lower horizontal tangent and a vertical tangent gave a cac of 1.38 mg/ml ~ 0.138 g/100 ml ~ 0.138 wt%.

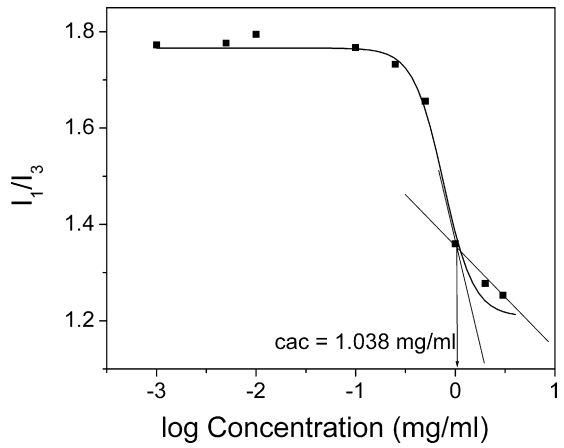


Fig. 4. Determination of critical aggregation concentration (cac) for CMP10-5 at 25 °C.

3.5. Viscometry

We show in Fig. 5(a), the concentrations dependence of viscosity for CMG, CMP10-5 and CMP10-10 at 25 °C. The viscosity of CMG increases gradually with increase in concentration with the incorporation of PNIPAm, there was a significant increase in viscosity as compared to the unmodified precursor, CMG. Especially, above C_p = 10 g/L there was a sharp increase in case of CMP10-5. The concentration, C_p = 10 g/L could be considered as the overlap concentration (C_p^*) above which the intermolecular hydrophobic associations play a major role in enhancing the viscosity. However, with CMP10-10 we observe a decrease in viscosity which could be due to the more hydrophobic nature of the sample.

We show in Fig. 5(b) the temperature dependence of the reduced viscosity for CMG, PNIPAm, CMP10-5 and CMP10-10. The reduced viscosity of CMG was not much affected by the temperature and there was only a slight decrease in viscosity with increasing temperature.

However, with the incorporation of PNIPAm side chains into CMG (sample CMP10-5) the reduced viscosity increased significantly which would be attributed to the formation of hydrophobic associations from PNIPAm chains. With further increase in PNIPAm content (CMP10-10), the viscosity decreased due to increased hydrophobicity of PNIPAm.

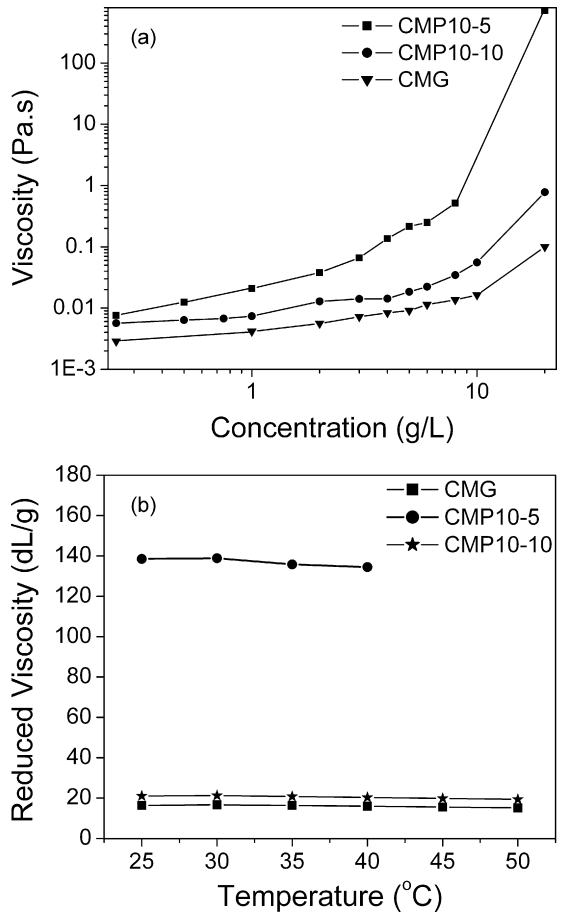


Fig. 5. (a) Concentration dependence of viscosity for CMG, CMP10-5 and CMP10-10 at 25 °C. (b) Temperature dependence of reduced viscosity in water for CMG, CMP10-5 and CMP10-10.

3.6. Oscillatory measurements

Mostly, the viscoelastic properties of associating polymer solutions have been described in terms of transient network theory (Macosko & Larson, 1994; Tanaka & Edwards, 1992; Wang, 1992). The theory explains the real (G', storage modulus) and imaginary (G'' loss modulus) parts of the complex viscoelastic shear modulus in terms of Maxwell model, which is expressed by the following equations,

$$G' = G_0 \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \quad (1)$$

$$G'' = G_0 \frac{\omega\tau}{1+\omega^2\tau^2} \quad (2)$$

where G_0, τ and ω are the plateau modulus, the relaxation time of the network and the angular frequency respectively. The plateau modulus, G_0 is given by

$$G_0 = \overset{368}{\underset{369}{\upsilon kT}} \quad (3)$$

where υ gives the elastically active chains per unit volume and k and T are Boltzmann constant and absolute temperature respectively.

In order to understand the viscoelastic nature of the CMG-g-PNIPAm copolymers, we performed oscillatory measurements on a typical sample of CMP10-5 at moderate concentrations.

Fig. 6 shows the typical frequency dependence of dynamic moduli (G' and G'') obtained with an aqueous solution of CMP10-5 at C_p = 10 g/L and 20 g/L. At low frequency, $G' < G''$ and the complex moduli did not follow the Maxwellian behavior since the slopes for G'' and G' are far away from 1 and 2 respectively. This indicates that there could be multimode relaxation process in the system. At higher frequencies, G' and G'' cross over at a characteristic frequency (ω_c = 39.8 rad/s for C_p = 10 g/L; ω_c = 7.85 rad/s for 20 g/L) which is related to the relaxation time of the network: $\tau = 1/\omega_c$. It can also be seen from the figure that, as the concentration increases, the 'ω_c' decreases and accordingly the relaxation time 'τ' increases. This is in line with the property that the thicker gels relax slower due to restricted molecular motion.

We also performed oscillatory measurements on sample CMP10-5 with C_p = 10 g/L at various temperatures and the cross over frequency, ω_c was determined as a function of temperature. Fig. 7 shows the decrease in ω_c with increase in temperature. This indicates that at higher temperature the thermoassociations prevail which lead to slow relaxation of the gels.

Estimation of 'E_a' from the TTS gives the characteristic time scale for the associations in these polymers. The activation energy can be

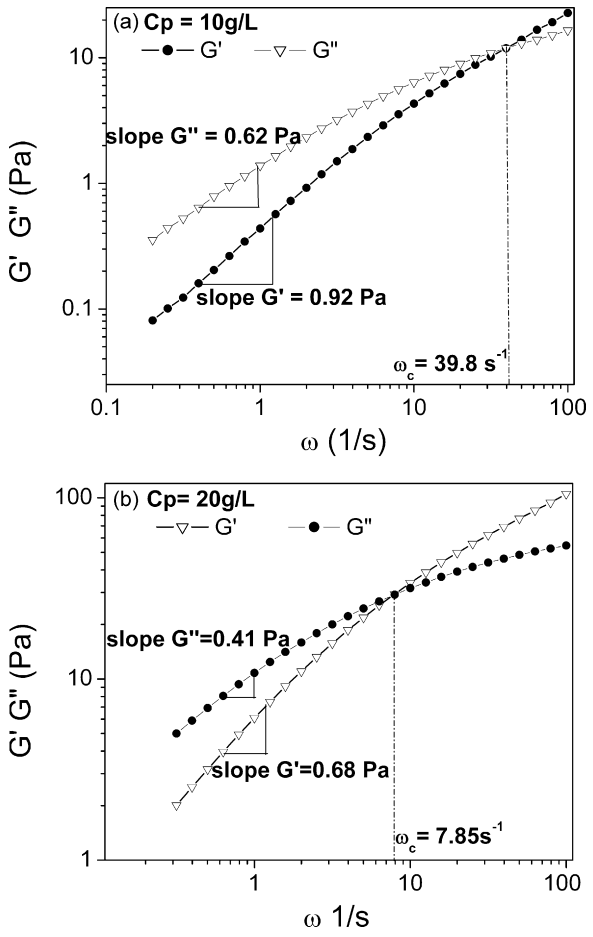


Fig. 6. The plots of storage modulus (G') and loss modulus (G'') versus frequency for CMP10-5 at 25 °C (a) C_p = 10 g/L and (b) C_p = 20 g/L.

estimated from the relaxation time (τ) which is given as,

$$\tau = \tau_0 \ \exp\left(\frac{E_a}{kT}\right) \quad (4)$$

where 'E_a' is the activation energy and τ_0 is the microscopic time corresponding to the diffusion of associating groups. The dynamic frequency sweep (DFS) measurements were performed on CMP10-5 (20 g/L) at different temperatures (T = 15, 20, 25 and 30 °C) and

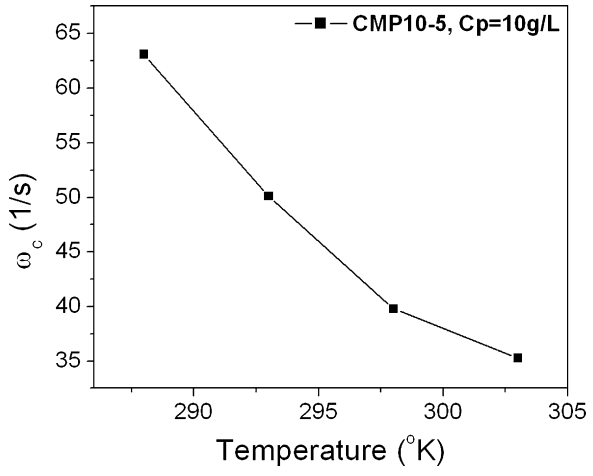


Fig. 7. The plot of cross over frequency (ω_c) as function of temperature for CMP10-5 (C_p = 10 g/L) from the oscillatory shear measurements.

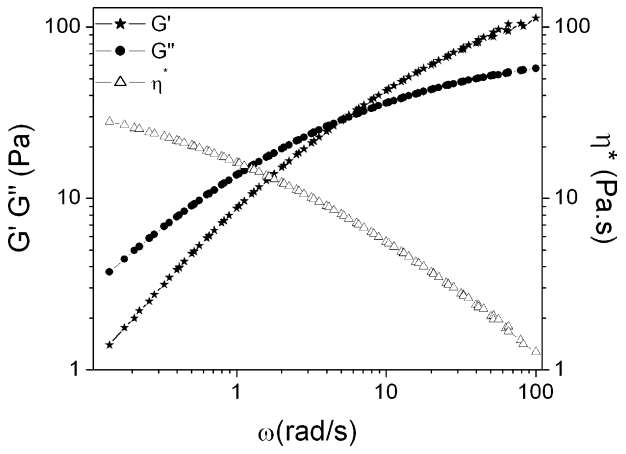


Fig. 8. Time–Temperature superposition for CMP10-5 with a reference temperature of 15 °C for the calculation of activation energy, E_a.

a TTS was applied to the data. A master curve obtained is given in Fig. 8 using a reference temperature, T_{ref} = 15 °C.

It can be seen from Fig. 8 that, the TTS procedure allows the superpositions of viscoelastic data by applying a frequency shift factor (a_T) and a modulus shift factor (b_T). The activation energy (E_a) determined experimentally in the temperature range of 15–30 °C is of the order of 21.2 J/mol which is consistent with the values reported earlier for similar system (Durand & Dellacherie, 2006; Tam, Farmer, Jenkins & Bassett, 1998).

4. Conclusion

The graft copolymers, CMG-g-PNIPAm prepared by coupling semitelechelic PNIPAm-NH_2 and CMG exhibited thermoresponsive behavior which was evidenced by the pyrene emission fluorescence measurements. Although the viscosity of CMG was increased upon the hydrophobic modification using PNIPAm, the thermo-thickening behavior was not observed. At moderate concentrations ($C_p \sim$ 10–20 g/L), the graft copolymer in water exhibited soft gel like nature and the viscoelastic properties (storage modulus, $G'$and loss modulus, G'') were studied using oscillatory shear experiments. The activation energy, E_a of association was estimated from the TTS. The gel like property of these polymers along with the biodegradable nature of CMG makes them as promising materials for the applications in industrial thickening systems.

Acknowledgements

N.R. Gupta is grateful to CSIR, New Delhi for the Senior Research Fellowship (SRF). The financial support from DST, New Delhi is also gratefully acknowledged.

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