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Effects of Tacticity and Molecular Weight of Poly(*N*-isopropylacrylamide) on Its Glass Transition Temperature

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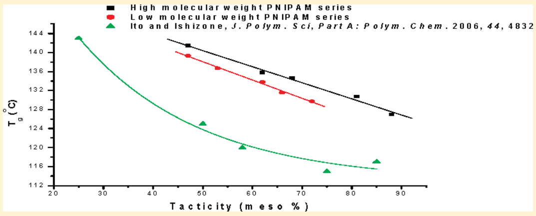
Supporting Information

ABSTRACT: A series of high molecular weight poly(*N*-isopropylacrylamide) (PNIPAM)s with low polydispersity ($M_n = 7.0 \times 10^4$ to 10.2×10^4 g mol^{-1}, PDI = 1.23−1.35) having different isotacticity [meso diad (m) = 47−88%]] was successfully synthesized using the reversible addition−fragmentation chain transfer (RAFT) polymerization method in the presence of different concentrations of $Y(OTf)_3$ Lewis acid. Measurement of the glass transition temperature (T_g) of this high molecular weight isotactic PNIPAM series and the low molecular weight PNIPAM series ($M_n = 3.5 \times 10^4$ to 4.0×10^4 g mol^{-1}, PDI = 1.2−1.3) having different isotacticity [meso diad (m) = 45−72%)] reported earlier by us (Ray et al. Polym. J. 2005, 37, 234) showed that T_g of PNIPAM decreases with increase in its meso diad content (m %) and decrease in its molecular weight.



Poly(*N*-isopropylacrylamide) (PNIPAM) is most widely studied thermo-responsive polymer due to its interesting thermal behavior. It undergoes volume phase transition (from coil-to-globular state) in water at around 33 °C. This temperature is known as its lower critical solution temperature (LCST).[1] Several efforts have been made to understand its phase behavior in water.[2−5] We reported the synthesis of stereo and molecular weight controlled PNIPAM using the reversible addition−fragmentation chain transfer (RAFT) polymerization in the presence and absence of Lewis acids.[6,7] Using the same technique, we also reported[8] the synthesis of a series of PNIPAM samples with different meso diad (m) values in the range of 45−72% having molecular weight (M_n) of 37 000 ± 3000 g mol^{-1} and polydispersity (M_w/M_n) in the range of 1.2−1.3 and the effect of tacticity of PNIPAM on the phase separation temperature of its aqueous solution. There are some more reports regarding the effect of tacticity on the temperature responsiveness of PNIPAM in its aqueous solution[9−11] as well in its nonaqueous solution.[12] But, there were very few reports regarding the study of the effect of tacticity of PNIPAM on its glass transition temperature (T_g).[9,13,14] Hirano et al.[9] revealed that the T_g value of syndiotactic PNIPAM having molecular weights (M_n) in the range 2.55×10^4 to 8.87×10^4 g mol^{-1} with PDI in the range 1.4−1.6 decreased linearly with increase in its r diad contents in the range of 53−71%. Ito and Ishizone[13] reported the T_g of stereoregular PNIPAMs having comparable molecular weights (M_n = 8500−11000 g mol^{-1}) with narrow PDI in the range 1.10−1.21. They observed that polymer with high m diad contents in the range 75−85% have T_g in the range 115−122 °C, although they did not observe any regular trend. They also observed that polymer with high r diad contents in the range of 75−83% have T_g in the range 143−148 °C. Recently, Nuopponen et al.[14] reported the effect of tacticity of stereoblock copolymers of PNIPAM on its T_g. However, they did not study in detail the effect of tacticity on T_g.

So far, to our knowledge, there was no other report regarding the tacticity effect on the glass transition temperature of PNIPAM. Here, we report the effect of tacticity on glass transition temperature of PNIPAM using two series of well-defined PNIPAMs of low molecular weights ($M_n = 3.5 \times 10^4$ to 4.0×10^4 g mol^{-1}, PDI = 1.2 - 1.3) and high molecular weights ($M_n = 7.0 \times 10^4$ to 10.2×10^4 g mol^{-1}, PDI = 1.23−1.34) of different isotacticity (m = 47−88%) and explore the effects of isotacticity and molecular weight of PNIPAM on its glass transition temperature.

PNIPAM samples of different isotacticities were prepared by RAFT polymerization of NIPAM monomer in a methanol−toluene (1/1, v/v) mixture at 60 °C using 1-phenylethyl phenyldithioacetate (PEPD) as RAFT agent and 2,2′-azobis(isobutyronitrile) (AIBN) as initiator in the presence of different concentration of yttrium triflate [$Y(OTf)_3$] Lewis acid. NIPAM and AIBN were recrystallized from hexane and ethanol, respectively. PEPD was synthesized

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according to the literature.[15] Methanol was distilled over ignited calcium oxide. Toluene was distilled over sodium—benzophenone. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by a Younglin ACME 9000 gel permeation chromatograph in DMF at 70 °C with flow rate 0.5 mL/min on two polystyrene gel columns [PL gel 5 μm and 10^4 Å columns (300 × 7.5 mm)] connected in series to a Younglin ACME 9000 gradient pump and a Younglin ACME 9000 RI detector. The columns were calibrated against seven poly(methyl methacrylate) (PMMA) standard samples (Polymer Lab, PMMA Calibration Kit, M-M-10). The ^{1}H NMR spectra were recorded on a JEOL AL300 FTNMR (300 MHz). Monomer conversion was measured from the ^{1}H NMR spectrum of the polymerization mixture in DMSO-d_6 at room temperature by comparing the integration of the monomer C═C—H peak at around 5.7 ppm with the N—C—H peak area of the polymer and the monomer at around 4.1 ppm. The tacticity of PNIPAM expressed in terms of the percentage of meso diad (m) content was determined from the methylene proton peaks of the polymer at 1.2—1.8 ppm recorded in DMSO-d_6 at 130 °C. Glass transition temperature (T_g) measurement was performed with a Metler 832 DSC instrument under N_2 atmosphere. The instrument is calibrated with indium before use. The samples were first heated to 200 at 20 °C/min heating rate and held at this temperature for 10 min to remove the thermal history, followd by quenching to −20 °C. A heating rate of 10 °C/min was used for second heating run. The T_g was taken as the mid point of the heat capacity change in the second heating run.

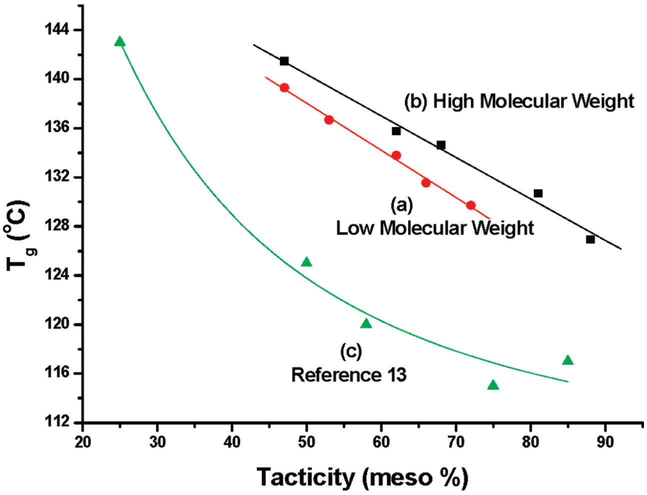

Figure 1. Comparison of glass transition temperature (T_g) with tacticity of (a) low molecular weight PNIPAM series, (b) high molecular weight PNIPAM series, and PNIPAMs reported in ref 13.

Plot of the T_g of five PNIPAM samples synthesized earlier[8] by us having molecular weight (M_n) in the range 3.5 × 10^4 to 4.0 × 10^4 g mol^{-1} with PDI in the range 1.2—1.3 (Supporting Information, Table S1) vs their corresponding isotactcity (% meso diad value, m) are shown in Figure 1a. It is clear from the figure that the glass transition temperature decreases linearly with increase in the isotacticity of PNIPAM.

In order to understand the effect of molecular weight on the T_g value of the PNIPAM polymer, we have prepared a series of PNIPAM samples of different isotacticities having high molecular weight (M_n) in the range 7.0 × 10^4 to 10.2× 10^4 g mol^{-1} with PDI in the range 1.23—1.35. Table 1 shows the corresponding conditions and results of polymerization and characterization of the formed polymers. High molecular weight PNIPAMs of different isotacticity with low PDI were successfully prepared using RAFT polymerization in the presence of different concentration of Y(OTf)$_3$ Lewis acid. Figure 1b shows the corresponding plot of the tacticity of PNIPAM samples vs glass transition temperature of the corresponding PNIPAMs. It is also showing the same behavior of decrease in T_g with increase in the meso diad value of PNIPAM. Glass transition temperatures of these polymers are higher than that of their low molecular weight homologues. For comparison, the plot of T_g data of PNIPAMs (M_n = 7600—11 000 g mol^{-1}, PDI = 1.10—1.21) reported by Ito and Ishizone[13] also included in Figure 1c. Here, also, with increase in the isotacticity, the corresponding observed T_g value decreases, although the rate of decrement is not consistent. However, Hirano et al.[9] also reported a linear dependence of T_g on the tacticity of PNIPAM series (M_n = 25 500—88 700 g mol^{-1}, PDI = 1.4—1.6) with m = 29—47%. Although all the polymers used in our present work have average polydispersity close to 1.27 ± 0.07, PDI of the polymer may have little effect on its T_g. Therefore, the major contributing factors are their molecular weight and isotacticity. Similar observation was also reported earlier in poly(methacrylates) systems.[16−27]

These observations may be explained as follows: with increase in the meso diad value of the PNIPAM, the number of side chains on the same side of the polymer backbone increases. Consequently, the intrachain interactions among the side chain groups [hydrogen bonding among amide groups and *van der Waals* (dispersion) forces among isopropyl groups] become stronger. As a result, the interchain interactions become weaker. Moreover, the possibility of chain entanglement will also be reduced. Indeed, Katsumoto et al.[12] showed that the interaction between the side chains of PNIPAM for the meso configuration is much stronger than that for the racemo one. Moreover, they showed that TG conformer of PNIPAM is most stable for meso configuration.

Table 1. Synthesis of High Molecular Weight Poly(N-isopropylacrylamide) of Different Isotacticity[a]

sample id	Y(OTf)$_3$ (M)	PEPD (mM)	time (h)	yield[b] (%)	M_n[c] (10^{-4}) (g mol^{-1})	M_w/M_n[c]	tacticity[d] (m/r)	T_g[e] (°C)
m-47	0	2.47	144	81	7.67	1.23	47/53	141.48
m-62	0.013	2.52	48	95	10.2	1.25	62/38	135.76
m-68	0.018	2.0	96	99	9.38	1.34	68/32	134.62
m-81	0.076	2.2	36	99	9.63	1.29	81/19	130.68
m-88	0.266	2.47	24	99	6.97	1.28	88/12	126.59

[a] [NIPAM] = 2.23 M, [AIBN] = 0.2 mM, Polymerization temperature = 60 °C, medium = 20 mL methanol—toluene (1:1, v/v) mixture. [b] Determined by ^{1}H NMR in DMSO-d_6 at 25 °C. [c] Determined by SEC (DMF, 0.5 mL/min, 70 °C, PMMA standard). [d] Determined by ^{1}H NMR in DMSO-d_6 at 130 °C. [e] Determined by DSC from second heating run with a rate of 10 °C/min.

Considering these, our quantum chemical calculations of PNIPAM (considering degree of polymerization, n = 6) at B3LYP/6-31G** level using Gaussian 03 suits of program[28] also indicate that the greater the meso (m) content of PNIPAM, the longer the helical sequence formed through sequential intrachain H-bonding between C═O and H−N of amide groups. When m tends to 100%, perfect helical structure is formed with C═O and H−N of amide groups at the inner circle of the helix and the isopropyl groups at the outer circle of the helix (Supporting Information, Figure S5). Under this condition, the possibility of chain entanglement is also feeble as the interchain interactions can only occur through weak *van der Waals* (dispersion) forces of isopropyl groups. With decrease in m values, perfect helical structure is gradually distorted as more and more C═O and H−N of amide groups are exposed toward the outer circle of the helix (e.g., Supporting Information, Figure S6, for m = 83%, and Figure S7, for m = 66%). Consequently, the possibility of chain entanglement through intermolecular H-bonding will also increase with concomitant weakening of the intramolecular H-bonding. As a result, there will be an increase in the interchain interactions with decrease in m value through weak *van der Waals* (dispersion) forces along with relatively stronger intermolecular H-bonding forces at the cost of intramolecular H-bonding forces. Therefore, the segmental motion of the polymer with higher meso diad value will occur at lower temperature with respect to its homologue having lower meso diad value.

At present, we conclude that the glass transition temperature of PNIPAM depends on its isotacticity value as well as on its molecular weight. Glass transition temperature of PNIPAM gradually decreases with increase in its isotacticity and with decrease in its molecular weight under the molecular weight range studied. These properties may find application in polymer blend and polymer processing studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Results of low molecular weight PNIPAM series, SEC charts, ^{1}H NMR spectra, DSC results of polymers, and quantum chemical calculation results of optimized structures of PNIPAMs having m = 100, 83, and 66%. This material is available free of charge via the Internet at http://pubs.acs.org.

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