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Studies on the Copolymerisation of N-Isopropyl-Acrylamide with Glycidyl Methacrylate

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Summary: The paper describes the homopolymerisation and copolymerisation of N-isopropyl acrylamide (NIPAM) with glycidyl methacrylate (GMA) in solution at 60°C using azobisisobutyronitrile (AIBN) as an initiator and dioxan as solvent. Copolymers were synthesized by varying the mol fraction of GMA in the initial feed from 0.025-0.125. All the polymerization reactions were terminated at low % conversion (10-15%) and the copolymer composition was determined by measuring the epoxy content. Percent epoxy content was determined by titration method using pyridine- HCl mixture. The reactivity ratios determined using Fineman-Ross method were found to be 0.94±0.05 (r_1, NIPAM) and 1.05±0.08 (r_2, GMA). All the polymers have high molecular weights with wide molecular weight distribution as determined by gel permeation chromatography (GPC) i.e. M_n in the range of 3.7×10^4 - 7.8×10^4 and M_w in the range of 1.2×10^5 - 4.1×10^5 with a polydispersity index in the range of 2.3-5.3. Lower critical solution temperature (LCST) of NIPAM homopolymer and copolymers was determined by recording DSC scans of polymers in aqueous solution. Incorporation of GMA in the poly(NIPAM) backbone resulted in a decrease in the LCST.

Keywords: copolymerization; glycidyl methacrylate; LCST; N-isopropyl acrylamide

Introduction

Copolymerisation is the most useful method for tailor making a polymer product with specifically desired properties. Copolymerisation modifies the symmetry of the polymer chain and modulates both intermolecular and intramolecular forces, so properties such as lower critical solution temperature (LCST), solubility etc of the smart polymer may be varied within wide limits. Polymers having transition temperature ranging from 3-150°C by using N-substituted acrylamides or methacrylamide as a monomer in the feed has been reported in the literature.[1-4] The cloud point of such polymers was strongly dependent on the polymer structure as well as on

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the copolymer composition. The greatest number of publication has been devoted to the polymers based on N-isopropylacrylamide, NIPAM, as both homo and copolymers of NIPAM can be easily obtained by free radical polymerization in aqueous and organic solvents. Although copolymerisaton of NIPAM with a variety of vinyl monomers is well reported in the literature however, no systematic study on the copolymerisation of NIPAM with functional monomer is reported.

In recent years, copolymers based on glycidyl methacrylate (GMA) have received increasing attention. The interest in these copolymers is largely due to the ability of pendant epoxide groups to enter into a large number of chemical reactions[5-7], thus offering the opportunity for chemical modification of the parent copolymer for various applications. For example, the copolymers based on glycidyl methacrylate has been used for binding enzymes and other biologically active species[8-9] and in electronic applications as negative electron beam resist. The high reactivity of the epoxide group is primarily due to the considerable strain in the three membered ring. The properties of homopolymer of GMA are largely affected by the polymerization method as well as by the microstructure in the copolymers. The objective of the present work was to combine the useful properties of NIPAM and functional monomer such as glycidyl methacrylate.

The present work was undertaken with an aim to investigate systematically the copolymerisation of NIPAM with varying mole fractions of GMA. Several copolymer samples were prepared by taking 0.025, 0.05, 0.075, 0.1 and 0.125 mole fractions of GMA in the feed. The rate of homopolymerisation of NIPAM /or GMA and copolymerisation of NIPAM: GMA (mole ratio 0.9:0.1) was investigated as a function of time, monomer concentration and initiator concentration. Copolymer composition was determined by measuring the epoxy group content in copolymers. LCST of these copolymers as determined by recording DSC scans in the presence of water decreased with increasing mole fraction of GMA in the copolymers. Thermal stability of the copolymers was determined by recording thermogravimetric traces in nitrogen atmosphere.

Experimental

Materials: N-isopropylacrylamide (NIPAM)(Aldrich), glycidyl methacrylate (GMA)(Fluka), petroleum spirit (Qualigens), methanol (Qualigens), N, N'- methylene bisacrylamide

(BAM)(Aldrich), potassium hydroxide (Qualigens) and sodium metal (S.D Fine chemicals) were used as such.

Azobisisobutyronitrile (AIBN) (High Polymer labs) and benzoyl peroxide (CDH) were recrystallised before use.

Homopolymerisation and Copolymerisation of NIPAM with GMA

Homopolymerisation and copolymerisation in nitrogen atmosphere of NIPAM and GMA at 60 ± 1°C was carried out in solution using AIBN as an initiator and dioxan as solvent.

A 20% w/v solution of NIPAM / GMA/ or required amounts of NIPAM : GMA mixture in dioxan was placed in a flask equipped with a magnetic stirrer, nitrogen inlet tube and reflux condenser. The temperature of the reaction mixture was raised to 60°C while passing nitrogen through it and then 0.5% (w/w) AIBN was added and the reaction was carried out for a desired interval of time, so as to keep the percent conversion below 15. The polymer was precipitated by slowly pouring the solution in to a beaker containing petroleum spirit. The polymer was isolated by filtration, purified by reprecipitating using dioxan /petroleum spirit. The polymers were then dried in vacuum oven at 60°C.

Five copolymer samples were prepared by varying the mole fraction of glycidyl methacrylate (GMA) from 0.025-0.125 in the initial feed. The samples have been designated as PNG followed by numerical suffix indicating the mole fraction of GMA multiplied by 100. For example, copolymers obtained by taking 0.025, 0.05, 0.075 and 0.125 moles of GMA have been designated as PNG–2.5, PNG-5, PNG-7.5 and PNG-12.5 respectively. Homopolymer of GMA and NIPAM have been designated as PG-100 and PN-100 respectively.

Rate of polymerisation

In order to determine the rate of hompolymerisaton and copolymerisation, solution polymerization reactions were carried out in nitrogen atmosphere at 60 ± 1°C for different intervals of time using 0.5% (w/w) AIBN as an initiator using dioxan as a solvent.

For copolymerisations, molar ratio of NIPAM : GMA (0.9:0.1 i.e sample PNG-10) were taken in the initial feed in three necked flask equipped with nitrogen inlet tube and water condenser. Dioxan was used as a solvent. After passing nitrogen for ~ 10 min and heating to 60°C, 0.5 % (w/w) AIBN was added to the continuously stirred reaction mixture. After desired interval of time, the contents of the flask were poured with continuous stirring into excess of petroleum spirit. The precipitated polymers were collected by filtaration followed by drying in vaccum oven at 50-60°C till constant weight. The weight of the polymer was used to calculate the % conversion.

The homopolymerisation and copolymerisation reactions were also carried out at 60 ± 0.1°C in N_2 atmosphere using different initiator concentrations i.e. 0.25, 0.5, 0.75 and 1.0 % (w/w) for studying the effect of initiator concentration on the rate of polymerization.

The effect of monomer concentration on the rate of polymerization was also investigated by keeping initiator concentration constant (0.5 % w/w) and taking 20 % (w/v) and 40 % (w/v) monomer concentration in the initial feed.

Characterization

Structural characterisation of the copolymers was done by recording FT-IR spectra in thin films using Perkin-Elmer 580B infra-red spectrophotometer.

The copolymer compositions were determined by estimating the epoxy group using pyridine-HCl method.

Intrinsic viscosity of the homopolymer and copolymers was determined in dioxan at 30 ± 0.1°C using Ubbelohde suspension level viscometer. Waters gel permeation chromatograph was used to determine molecular weight and molecular weight distribution.

Thermal characterization

DSC traces of homopolymers and copolymers in presence of water were recorded using TA 2100 thermal analyzer having 910 DSC module. A sample weight of 4±1 mg and 2 mg of water in DSC crucible (which were sealed to prevent the evaporation of water) were used for recording DSC traces at a heating rate of 5°C /min. The lower critical solution temperature (LCST) was recorded as the endothermic shift in the base line.

Thermal stability of the homopolymers and copolymers was evaluated by recording TG/DTG traces in nitrogen atmosphere in the temperature range of 50-800°C. A Dupont 2100 thermal analyzer having 951 TG module and a heating rate of 20°C /min was used for recording TG/DTG traces in nitrogen atmosphere. A sample weight of 10 ± 2 mg was used in each experiment.

Results and Discussion

Rate of polymerisation

For kinetic studies, homopolymerisation and copolymerisation of NIPAM: GMA (0.9:0.1,sample PNG-10) was carried out in nitrogen atmosphere for different intervals of time or at varying concentrations of initiator. The rate of polymerization may be influenced by (a) structure of monomers/comonomers (b) monomer concentration (c) initiator concentration and (d) temperature.

Effect of time and monomer concentration

The rate of homopolymerisation of NIPAM /GMA and copolymerisation of NIPAM:GMA (molar ratio 0.9:0.1 sample PNG-10) was followed gravimetrically. A linear increase in % conversion was observed in the homopolymerisation of NIPAM (sample PN-100), GMA (sample PG-100) and PNG-10 monomer concentrations of 20%(w/v) and 40%(w/v). As expected the rate of polymerization was found to be higher at 40%(w/v) monomer concentration in all the systems (Table 1).

Effect of initiator concentration

The effect of initiator concentration on the rate of polymerization was investigated by taking 0.25, 0.50, 0.75 and 1.0 % w/w of AIBN in the initial feed. The monomer concentration (20%) (w/v) and the reaction time (30 min) was kept constant to investigate the effect of initiator concentration. A plot of R_p vs $In^{1/2}$ for homopolymerisation of NIPAM or GMA and their copolymerisation (sample PNG-10) was found to be linear indicating thereby that the rate of polymerization was dependent on the half power of the initiator concentration. This implies that the termination was either by combination or disproportionate. No departure from polymerization kinetics explains the absence of side reactions especially primary radical termination.

Characterization of copolymers

In the FT IR spectra of copolymers a characteristic absorption band due to amide group of NIPAM at 1652 ± $1cm^{-1}$ and 1521 ± $1cm^{-1}$ and due to carbonyl and epoxy group of glycidyl at 1732 ±$1cm^{-1}$ and 909 ± 1 cm^{-1} respectively was observed. The epoxy content in the copolymers

Table 1. Effect of monomer concentration on the rate of polymerization

Sample Designation	Weight of monomers in feed (g)		Dioxan (ml)	Rp % conversion/min
	NIPAM	GMA		
PN-100	4	-	10	0.96
PN-100*	4	-	20	0.61
PG-100	-	4.0	10	0.33
PG-100*	-	4.0	20	0.281
PNG-10	4.068	0.568	11.6	0.72
PNG-10*	4.068	0.568	23.2	0.45

***** represents 20% (w/v) monomer concentration***

determined quantitatively by titration method was used to calculate the copolymer composition (Table 2). From the knowledge of copolymer composition, reactivity ratios were calculated using Fineman Ross and Kelen Tudos method and it was found to be 0.94 ± 0.05 (r_1) and 1.05 ± 0.08(r_2).

Molecular characterization

Intrinsic viscosity increased with increasing GMA content in the copolymers (Table 3). [η] is a measure of hydrodynamic volume and depends on the molecular weight as well as on the size of the polymer coil in solution. Increase in [η] with inceasing GMA content could be due to the better solvating power of dioxan. All the homopolymers and copolymers have high molecular weight i.e. M_n in the range of $3.7 \times 10^4 - 7.8 \times 10^4$ and M_w in the range of $1.2 \times 10^5 - 4.1 \times 10^5$ with polydispersity index in the range of 2.3-5.3.

Table 2. Details of feed composition and copolymer composition

Sample designation	Mole fraction of monomers in Feed		Epoxy content %	Mole fraction of GMA (m_2)
	NIPAM (M_1)	GMA (M_2)		
PNG 2.5	0.975	0.025	0.98	0.026
PNG 5.0	0.950	0.050	2.32	0.062
PNG 7.5	0.925	0.075	3.27	0.088
PNG 10	0.900	0.100	4.50	0.122
PNG 12.5	0.875	0.125	5.24	0.143

Thermal characterization

Fig 1 and 2 show the DSC scans of PN 100* of varying molecular weight and copolymers of varying composition respectively in the presence of water. An endothermic shift in base line due to phase transition, known as lower critical solution temperature (LCST) was observed in all the DSC scans. The endothermic transition was characterized by noting T_i (onset temperature), T_{mid} (LCST) and T_f (final temperature) and the results are summarized in Table 3. LCST of PN-100 was found to be in the range of 30.4-31.5 °C and was marginally affected by the molecular weight. LCST decreased with increasing amounts of GMA in the copolymers. This can be attributed to the hydrophobic nature of GMA which increases the hydrophobicity of the copolymers and lowers the phase transition temperature An increase /decrease in LCST upon copolymerisation of NIPAM with hydrophilic or hydrophobic monomers has already been reported in the literature. [4,5]

Table 3. Results of intrinsic viscosity and LCST (DSC traces recorded at a rate of 5°C/min)

Sample designation	[η] mL/g	T_i (°C)	T_{mid} (°C)	T_f (°C)
PN-100	12	29.9	30.9	31.5
PN-100	27	29.3	31.5	32.2
PN-100	29	29.1	31.1	32.0
PNG-2.5	14	24.4	28.63	30.20
PNG-5	21	24.0	27.27	30.00
PNG-7.5	48	23.10	27.00	29.90
PNG-10	62	14.60	20.00	23.00
PNG-12.5	133	-	-	-

Thermogravimetric analysis

The relative thermal stability of samples was compared by comparing the initial decomposition temperature (IDT), temperature of maximum rate of weight loss (T_{max}) and the final decomposition temperature (FDT) and the results are summarized in Table 4. A typical TG/DTG trace PNG-10 is shown in Fig 3. A weight loss of 5-13% was observed in the temperature range of 50-300°C in all the samples which may be due to the presence of absorbed and bound water. Major weight loss was observed in the temperature range of 300 to 800°C. The effect of molecular weight on the thermal stability of NIPAM homopolymer and NIPAM-GMA

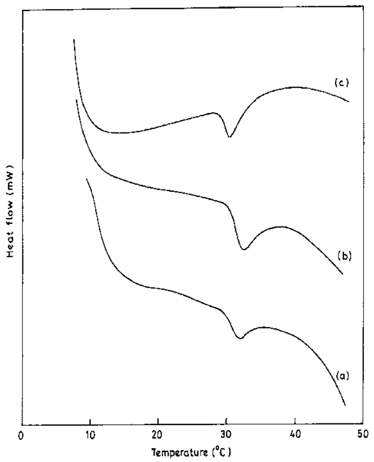

Figure1. DSC traces of PN*- 100 at varying % conversion (a)3.4 (b) 29.4 (c) 38.1

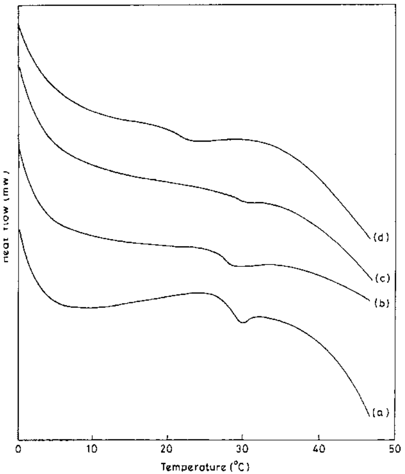

Figure 2. DSC traces of copolymers (a) PNG-2.5 (b) PNG-5 (c) PNG-7.5 (d) PNG-10

copolymer i.e. PNG-10 was also investigated. As expected thermal stability of homopolymer was independent of molecular weight, whereas in copolymer (PNG-10), an increase in IDT, T_{max} and FDT was observed. An increase in these temperatures with % conversion in copolymer could be due to the change in copolymer composition or due to the microstructural changes. The varying mole fraction of GMA showed a similar thermal behaviour with slight variation of IDT, T_{max} and FDT values.

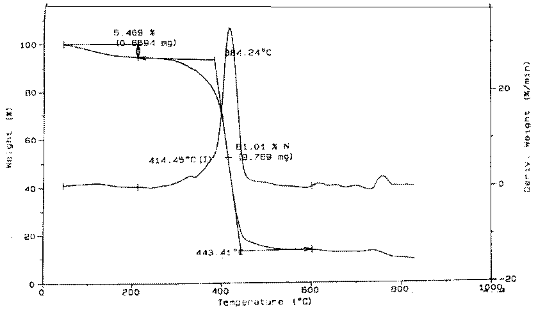

Figure3. TG/DTG trace of PNG-10

Table 4. Results of thermogravimetric analysis of homopolymers and copolymers (Heating rate 20°C/min, N_2 atmosphere)

Sample designation	% Conversion	[η]	IDT (°C)	T_{max} (°C)	FDT (°C)
PN-100	27.23	22.9	415.4	437.5	450.3
PN-100	65.69	50.0	417.1	440.6	449.9
PG-100	10.42	39.0	406.5	425.0	441.9
PG-100	29.82	91.5	411.6	428.1	446.6
PNG-2.5	8.76	14.0	395.2	418.8	433.4
PNG-5.0	10.92	21.0	396.1	428.1	449.9
PNG-7.5	11.56	48.0	389.1	415.6	445.1
PNG-10	12.12	54.0	384.2	413.3	443.4
PNG-10	22.16	62.0	408.9	425.0	438.6
PNG-10	32.15	70.4	414.3	435.5	445.0
PNG-12.5	14.85	133.2	411.5	431.3	445.2

Conclusion

Incorporation of small amounts of GMA can be used to introduce functional group in the polymer backbone without much affecting the LCST.

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