

AIBN initiated free radical homopolymerization of *N*-(1-naphthyl)maleimide and copolymerization with MMA : synthesis and characterization

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Manuscript received 14 November 2007, accepted 3 April 2008

Abstract : Free radical homopolymerization of *N*-(1-naphthyl)maleimide (NMI) and copolymerization with MMA were performed in THF at 65 °C with AIBN as the initiator. Nine copolymer samples were prepared using different feed ratios of comonomers. The prepared polymer sample have been characterized by solubility test, intrinsic viscosity, FT-IR and ¹H NMR spectral analysis. The thermal properties have been studied by thermo-gravimetric analysis.

Keywords : *N*-(1-Naphthyl)maleimide, AIBN, polymerization, TGA.

Introduction

At present there is a considerable interest not only in the synthesis of new types of plastic materials, but also in the modification of commodity polymers in order to improve their properties to meet requirement for new applications. One of the existing methods of improving polymer properties is the copolymerization¹.

Polyimides-related polymers exhibited excellent thermal stability and electrical properties, as well as chemical resistance. Such type of polymers have been widely used²⁻⁵. Most aromatic polyimides generated by the thermal solid-state phase imidization show insolubility and infusibility, which make processing difficult. These undesirable properties, which limit the vast applications of the polyimides, are due to their chain rigidity as well as poor by defined molecular architectures. Addition type polyimides were developed mainly to overcome processing disadvantages⁶⁻⁸. During the past several years many publications appeared describing the chemical modification of various vinyl polymers such as styrene, *n*-butyl acrylate, vinyl chloride, acrylonitrile, ethyl phenyl acrylate, cyclohexene and MMA by an addition of *N*-substituted maleimide⁹⁻²¹.

We report here the synthesis of monomer, *N*-(1-naphthyl)maleimide (NMI) and its polymerization and copolymerization with MMA. It was found that such copolymers have better thermal stability than the polymers of vinyl monomers. Studies of physical, spectral and thermal properties have been carried out in order to charac-

terize the polymers. The effects of different feed ratios of monomers on the properties of copolymers have been examined.

Results and discussion

Intrinsic viscosity (η) :

Intrinsic viscosity (η) is a measure of hydrodynamic volume and depends on molecular weight, as well as on the size of the polymer coil in a given solution. The values (η) in DMF solution at 30 °C are listed in Table 1. The value of (η) decreased as the content of NMI increased.

Table 1. Radical polymerization and copolymerization of H-NMI with MMA in THF at 65 °C

Polymer code	Feed mol fraction of NMI	Polymerization time (h)	Yield (%)	%N	[η] dl/g	Appearance
H-NMI	1.0	48	44.55	6.03	0.039	Brown
C-NMI	0.5	36	52.35	4.02	0.049	Yellow

Solubility behaviour :

The solubilities of the homo and copolymer samples were determined in polar and non-polar solvents and have been summarized in Table 2. The H-NMI and C-NMI are completely soluble in acetone, dioxane, THF, DMSO, DMF, ethyl acetate, chloroform, dichloromethane, benzene and toluene. The homopolymer is insoluble in carbon tetrachloride, while the copolymer is soluble in car-

bon tetrachloride. Both H-NMI and C-NMI are partially soluble in cyclohexanone and 1-butanol. The solubility behaviour of the homo and copolymer depends on the composition of the polymer.

Table 2. Solubility behaviour of monomer, homopolymer and copolymer in polar and non-polar solvents at 30 °C

Solvent	NMI	H-NMI	C-NMI
THF	S	S	S
DMF	S	S	S
DMSO	S	S	S
Acetone	S	S	S
Dioxane	S	S	S
Ethyl acetate	PS	S	S
Cyclohexanone	S	PS	PS
Chloroform	S	S	S
Benzene	S	S	S
Toluene	S	S	S
Dichloromethane	S	S	S
CCl ₄	IS	IS	S
1-Butanol	S	PS	PS

PS = Partially Soluble, IS = Insoluble, S = Soluble.

Spectral characterization :

The FT-IR spectrum (Fig. 6) and ¹H NMR spectrum (Fig. 1) (400 MHz in DMSO-*d*₆) of H-NMI have the following peaks and chemical shift values.

The absence of a sharp band at 960 cm⁻¹ and chemical shift δ 7.32 ppm due to CH=CH in a monomer having a vinyl group, such as monomer NMI, indicate the formation of polymer through vinyl group polymerization^{22,23}. The IR spectra shows the characteristic peak at 3054 cm⁻¹, (CH=CH stretching). 1777 cm⁻¹, 1714 cm⁻¹ due to symmetric and asymmetric stretching of C=C in a five member imide ring indicated that the imide ring was involved in the polymerization. The imide group is also confirmed from the observed band at 1371 (Ar-N stretch), 1190-1096 (C-O-C stretch). 796 and 625 cm⁻¹.

The δ observed at 7.13-7.20 ppm due to CH=CH in the monomer had shifted to 3.50-4.12 ppm in the homopolymer, as a result of the formation of a semi flexible poly(substituted methine) [CH-CH]_n group²⁴. The δ for methine (CH-CH) proton has been reported in the range from 3.0-5.0 ppm depending on the substitution in maleimide. The value of δ in the range 3.0-4.0 for poly [*N*-[4-(*N'*-benzyl-aminocarbonyl)phenyl]maleimide²⁵, has been reported. The broad peak at 7.0-8.1 ppm corresponds to 9 aromatic protons.

The major characteristic absorption bands in FT-IR spectra (Fig. 5) are observed at 3150-2951 (aromatic, C-H stretch), 1721, 1770 (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1602, 1535 (C=C stretch, aromatic), 1487, 1444 (C-H band, -CH₂), 1352 (due to overlapping of C-N stretch and C-H band of -CH₃ group). These characteris-

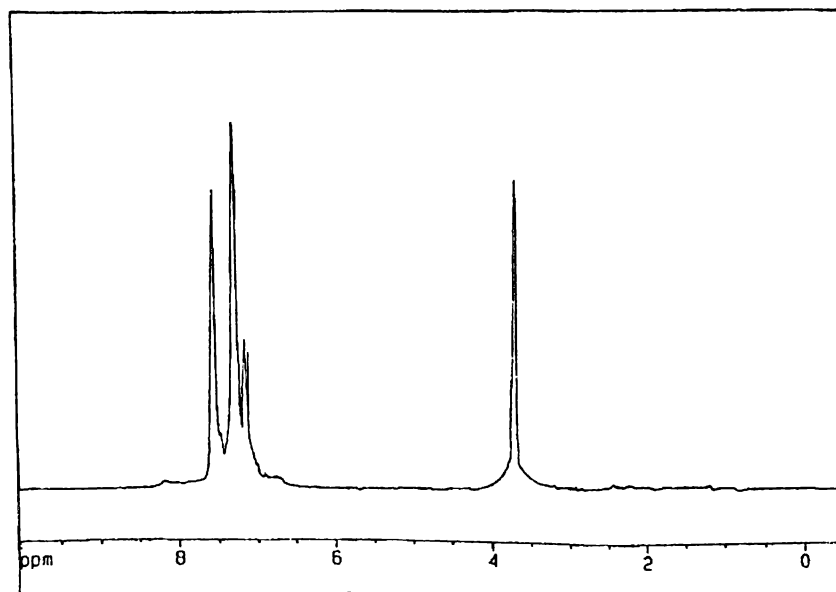
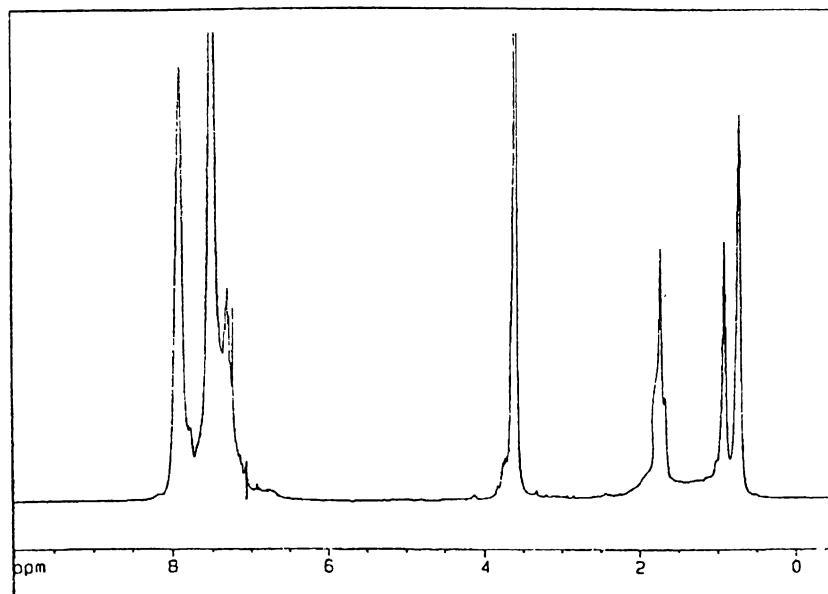


Fig. 1. ¹H NMR spectra of H-NMI.

Fig. 2. ^1H NMR spectra of C-NMI.

tic bands confirm that units of both the monomers NMI and MMA are present in the copolymer samples.

The ^1H NMR spectra (Fig. 2) of the copolymer sample showed the following chemical shifts. The δ value observed for 7 aromatic protons was at 7.25–8.10 ppm. The chemical shifts δ for $-\text{CH}-\text{CH}-$ and $-\text{OCH}_3$ are observed around 3.60–3.93 ppm. For 2H ($-\text{CH}_2-$) δ was observed at 1.90–2.10 ppm and for three $-\text{CH}_3$ protons was observed around δ 0.72–1.34 ppm.

Thermal properties :

It is well known that polymaleimide is potential heat and chemical resistant; therefore maleimide is very useful for improving the polymeric properties. Only single step degradation at temperature over 300 °C was observed for polymaleimide in TGA. The thermograms were obtained by heating the homopolymer and copolymer samples in air (10 °C/min).

The results of percentage weight loss suffered from 100 °C to 600 °C at 100 intervals are furnished in Table 4. The initial decomposition temperature T_i , temperature for maximum weight loss T_{max} and final decomposition temperature T_f are given in Table 3.

Table 3. Thermal behaviour of homo and copolymers

Polymer	T_i (°C)	T_{max} (°C)	T_f (°C)	Residue at 600 °C (%)
H-NMI	200	400	550	7.83
C-NMI	190	300	550	13.43

Table 4. Percentage weight loss of homo and copolymer at various temperatures from the TGA

Polymer	200 °C	300 °C	400 °C	500 °C	600 °C
H-NMI	1.48	18.96	88.17	90.94	96.30
C-NMI	11.10	73.48	79.34	83.08	86.57

The results in Table 3 indicate that the relative thermal stability on the basis of T_i follows the order H-NMI > C-NMI. The thermogram (Fig. 3) of H-NMI shows the single step degradation. Initial degradation from 200 °C involving about 1.48% weight loss, 18.96% at 300 °C, 88.17 at 400 °C, 90.94% at 500 °C and 92.17% weight loss at end of 550 °C.

The thermogram (Fig. 4) of copolymer shows the step-by-step degradation. In copolymer initial weight degradation from 190 °C, involving about 6.99% weight loss, 11.10% at 200 °C, 73.48% at 300 °C, 79.34% weight loss at 400 °C and 86.57% weight loss at the end of 550 °C.

Experimental

Materials :

Maleic anhydride (SRL, extra pure) was first recrystallized from chloroform and then further purified by sublimation at 54 ± 2 °C. 1-Naphthylamine (SRL, pure) and P_2O_5 , H_2SO_4 (SRL, A.R.) were used as received. MMA (SRL, A.R.) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over

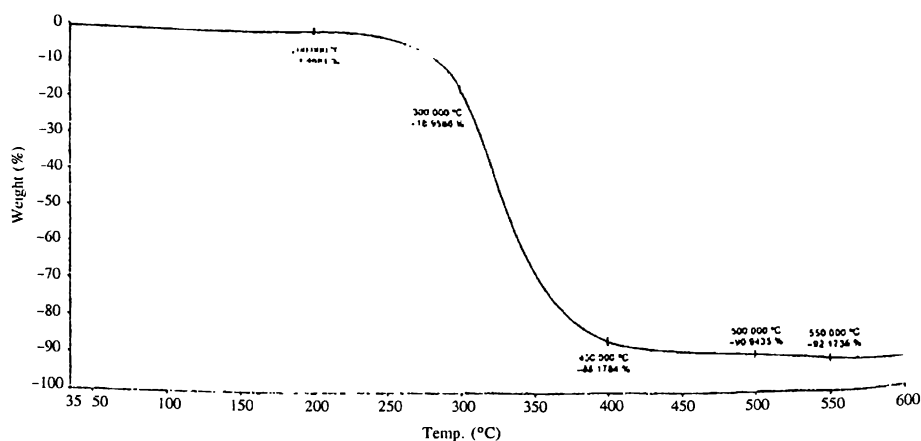


Fig. 3. Thermogram of H-NMI.

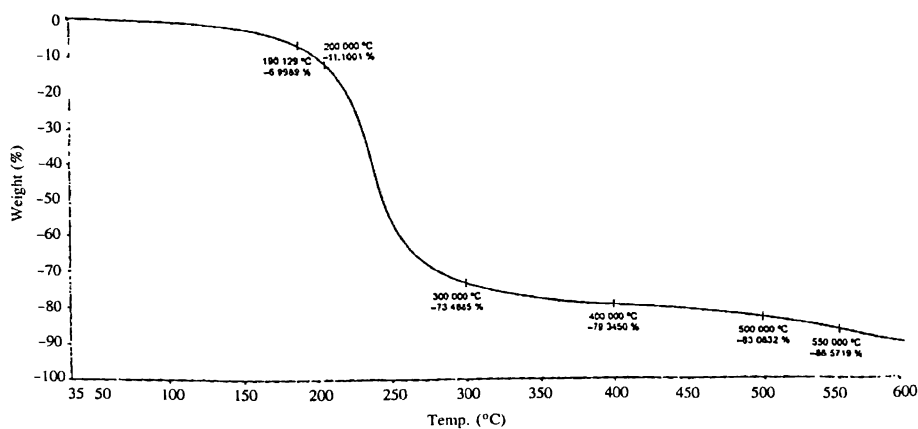


Fig. 4. Thermogram of C-NMI.

anhydrous CaCl_2 for 6 h and distilled¹⁶. The head and tail fractions were discarded. AIBN (Spectrochem) was recrystallized twice from methanol prior to use. DMF, THF, dichloromethane etc. used in the present work were of analytical grade and of purity better than 99 mol %, and were used as received. THF was purified by distillation after being refluxed for 2 h in the presence of sodium¹⁶.

Measurements :

^1H NMR spectra of polymer samples were taken in $\text{DMSO}-d_6$, on a Bruker-Vance spectrometer at 400 MHz. The internal reference used was TMS. FT-IR spectra of the polymer samples were recorded on a Perkin-Elmer IR spectrometer, using a KBr pellet technique. The viscosity measurements were carried out in DMF at 30 ± 0.1 °C, using an Ubbelohde suspended level viscometer.

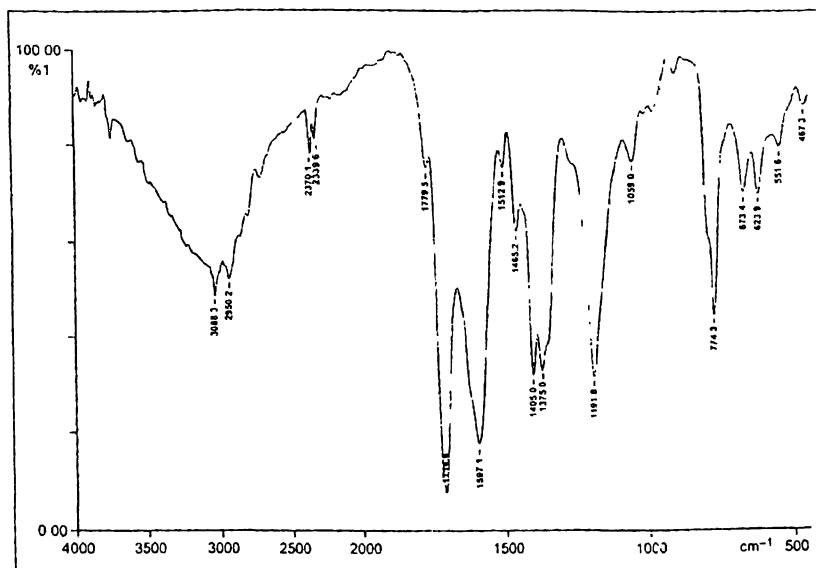


Fig. 5. IR spectra of C-NMI.

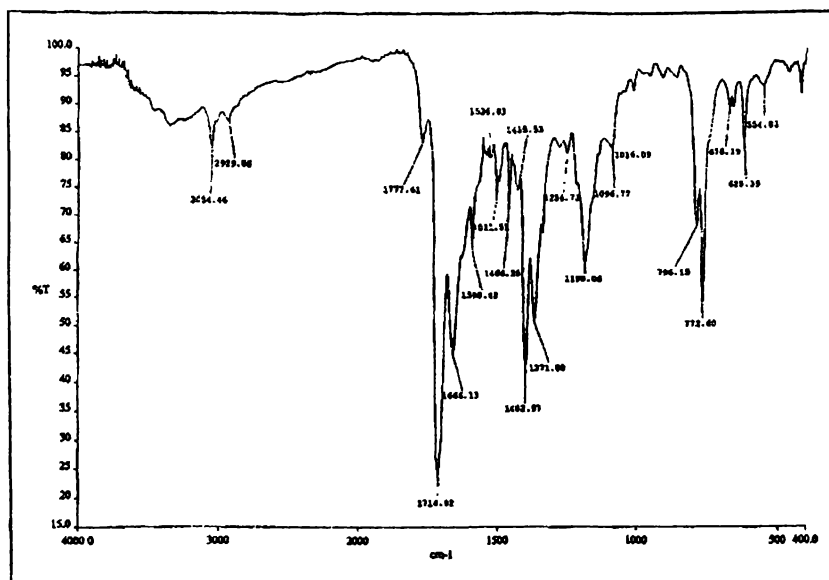


Fig. 6. IR spectra of H-NMI.

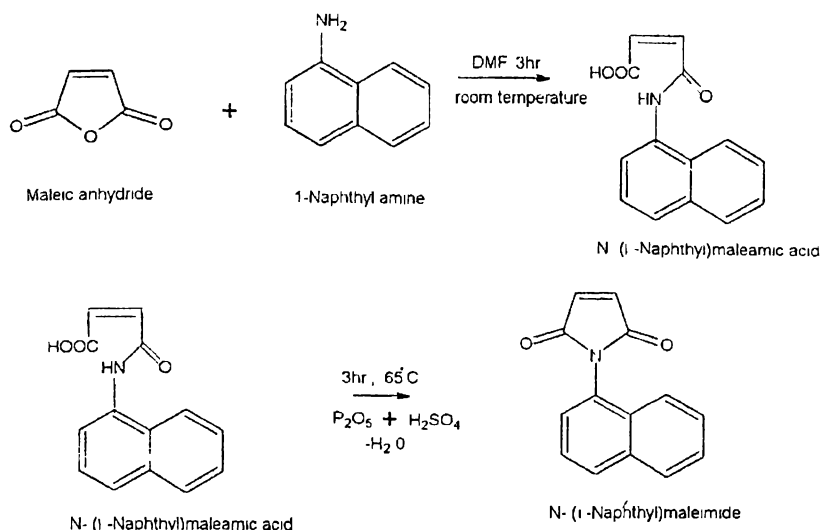
Elemental analysis was made on a Carlo Erba Model Na 500 series analyzer. The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of 10 °C/min.

Preparation of N-(1-naphthyl)maleimide (NMI) :

The monomer *N*-(1-naphthyl)maleimide (NMI) has been prepared in two steps from maleic anhydride and α -naphthylamine.

Synthesis of N-(1-naphthyl)maleamic acid (NMA) :

The solution of maleic anhydride (9.81 g, 0.1 mol) in DMF was gradually added over a period of 15 min to a well-stirred solution of α -naphthylamine (14.3 g, 0.1 mol) in DMF. The solution was stirred for 3 h at room temperature. The solution was poured into crushed ice or cooled water. Yellow precipitate of NMA was obtained. The precipitate was filtered and dried at 55 °C and then recrystallized from dichloromethane to obtain pure NMA in a 90% yield (m.p. 120 °C).



Scheme 1

The IR spectrum showed absorption at 3464–3170 (carboxylic acid O–H), 3321, 1537, 1504 (amide N–H), 1294 (carboxylic acid C–O), 830 (CH=CH), 675 (C–H bending) in cm^{-1} .

Synthesis of N-(1-naphthyl)maleimide (NMI) :

N-(1-Naphthyl)maleamic acid 24.1 g (0.1 mol) in 70 ml DMF was taken in a flat round-bottomed flask. The solution was treated with conc. H_2SO_4 and P_2O_5 . The whole solution was stirred for three hours. The resulting solution was poured in cooled water and a greenish yellow precipitate was obtained. It was recrystallized from dichloromethane. Yield was 70%, m.p. 140°C . The IR spectrum showed absorptions at 1782–1705 (asymmetric and symmetric stretching of C=O in a five member imide ring)^{10–12}, 1507, 1595, 1405 (C=C, aromatic)^{7–9}, 1368 (C–N stretch)⁹, 936 (CH=CH)^{15,26} cm^{-1} .

^1H NMR spectra of NMI indicated (a) two methine (CH=CH) protons at δ 7.20 (s) ppm⁶ and (b) two phenyl protons at 7.34–7.80 (m) ppm.

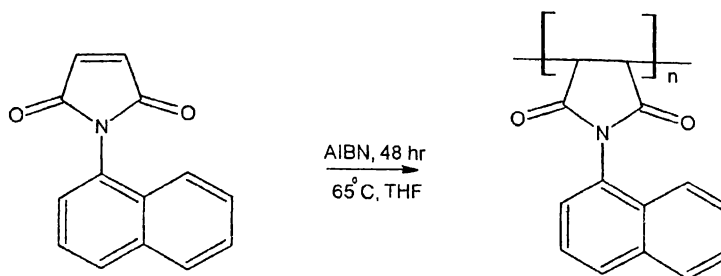
Polymerization :

Homopolymerization :

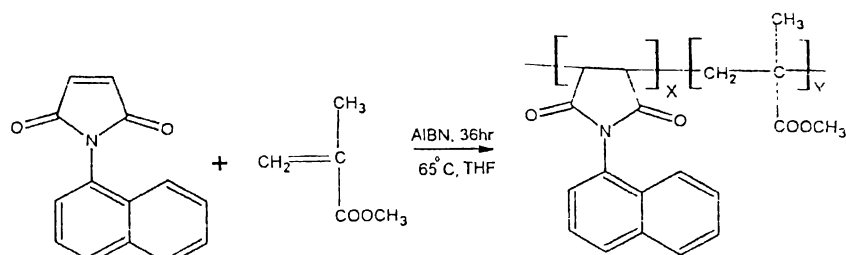
N-(1-Naphthyl)maleimide (2.23 g for 0.01 mol) and 30 ml THF were taken in a flat round-bottomed flask and the initiator AIBN was added. The solution was refluxed for 48 h at 65°C . The homopolymer (H-NMI) was isolated by using an excess quantity of methanol water mixture. The crude H-NMI was purified by dissolving it in THF and precipitating from a methanol water mixture. It was dried under vacuum at 60°C . The homopolymerization was carried out for different time and the yield are given in Table 5.

Table 5. Effect of time on homopolymer yield homopolymer

Code	Time (h)	Yield (%)	State	Appearance
H-NMI	24	39.45	Solid	Brown
	36	41.61	Solid	Brown
	48	44.45	Solid	Brown



Scheme 2



Scheme 3

Copolymerization :

The copolymerization was carried out at 65 °C for 12, 24, 36 and 48 h, employing calculated amount of comonomers MMA and NMI in 35 ml THF with 100 mg AIBN. The copolymer was isolated from an excess quantity of methanol containing water. After dissolving the crude copolymer in THF, it was precipitated from an excess quantity of methanol water mixture. The process was repeated three times to purify the copolymer sample. The precipitated copolymer was washed with methanol several times and dried at 60 °C under vacuum. The nine copolymer samples were prepared using different feed

ratio of comonomers. The physical properties and yields are listed in Table 6. Copolymerization was carried out for different time and yield are given in Table 7.

Table 6. Radical polymerization and copolymerization of NMI and MMA in THF at 65 °C

Polymer code	Feed ratios NMI : MMA	Polymer time (h)	Yield (%)	State	Appearance
C-NMI-1	1 : 9	12	34.2	Viscous liquid	Light yellow
C-NMI-2	2 : 8	12	34.0	Viscous liquid	Light yellow
C-NMI-3	3 : 7	12	35.0	Viscous liquid	Light yellow
C-NMI-4	4 : 6	12	36.0	Solid powder	Yellow
C-NMI-5	5 : 5	12	38.0	Solid powder	Yellow
C-NMI-6	6 : 4	12	25.0	Solid powder	Yellow
C-NMI-7	7 : 3	12	37.0	Solid powder	Yellow
C-NMI-8	8 : 2	12	38.4	Solid powder	Yellow
C-NMI-9	9 : 1	12	39.4	Solid powder	Yellow

Table 7. Effect of time on copolymer yield

Polymer code	Feed mol ratios NMI : MMA	Polymer time (h)	Yield (%)	State	Appearance
C-NMI	0.1 : 0.1	12	22.20	Solid	Yellow
		24	40.50	Solid	Yellow
		36	52.35	Solid	Yellow
		48	54.46	Solid	Yellow

Conclusion :

Homopolymerization and copolymerization proceed through the free radical mechanism. The investigated poly and copolymaleimides show excellent solubility in THF, DMF, DMSO, dioxane, ethyl acetate, acetone and dichloromethane. The homo and copolymers were characterized by IR and ¹H NMR spectral analysis. Synthesized homopolymer show good thermal stability than the copolymer but other properties are improved in copolymerization.

Acknowledgement

We are thankful to CDRI, Lucknow and SICART, Vallabh Vidyanager for analysis work. We are also thankful to Prof. S. L. Oswal (South Gujarat University, Surat) for his valuable suggestions. One of the authors, Shiv Narayan Paliwal is thankful to UGC, New Delhi for financial assistance.

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