

SYNTHESIS AND CHARACTERIZATION OF 1-NAPHTHYLMETHYL METHACRYLATE- METHYL METHACRYLATE COPOLYMERS

CHEN Liusheng (陈柳生)

(*Institute of Chemistry, Academia Sinica, Beijing*)

WANG Guochang (王国昌)

(*Institute of Polymer Chemistry, Nankai University, Tianjin*)

and Mitchell A. Winnik

(*Department of Chemistry, University of Toronto, Canada*)

ABSTRACT

A series of 1-naphthylmethyl methacrylate (NMMA)-methyl methacrylate (MMA) copolymers were synthesized on free radical mechanism. The reactivity ratios of NMMA (r_1) and MMA (r_2) were reported to be 0.83 and 0.89, respectively. The characterization of the copolymers by using IR, NMR, GPC, UV and fluorescence spectrometry was described in this paper.

It has been demonstrated that luminescence techniques are powerful methods for understanding polymer photolysis, structure and dynamics of polymers^[1-4] as well as microphase morphology and interface phenomena in polymer colloids^[5-7]. Some polymers labelled with naphthalene groups have been used to study the effects of naphthalene substituted position^[8,9], the composition^[10] and structure^[11-13] of the polymers on intramolecular energy migration and excimer formation. For further study of the effect of the copolymer composition on the photo-physical processes, a series of copolymers with various contents of naphthalene groups were synthesized. The objective of this report is concentrated on the study of the polymerization and characterization of these copolymers.

EXPERIMENTAL

Materials

Monomer, methyl methacrylate (MMA), was washed several times with diluent aqueous solution of sodium hydroxide followed by repeated water washing, dried over calcium chloride and then distilled under reduced nitrogen atmosphere. The medium fraction was collected, $n_D^{20}=1.4141$.

Monomer, 1-naphthylmethyl methacrylate (NMMA) was prepared by the condensation of 1-naphthalenemethanol (Aldrich) with methacryloyl chloride, which was distilled under reduced nitrogen atmosphere just before use. To a solution of 24.4 g naphthalenemethanol, 25 ml dry triethylamine and 125 ml toluene cooled below -5°C , 20 ml methacryloyl chloride was added over an hour under stirring. After stirring for additional 4 hours at $-5^{\circ}\sim 0^{\circ}\text{C}$, 100 ml ice water was added to dissolve the amine hydrochloride. The product was extracted out with diethyl ether, washed with aqueous HCl/saturated $\text{NaHCO}_3/\text{H}_2\text{O}$, dried over MgSO_4 and then filtered. Ether was evaporated off in a rotary evaporator. The crude product was purified by a 46 cm $\times$ i.d. 3 cm flash silica gel column (230–400 mesh, E. Merck) with a 3:1 mixture of benzene and hexane as elution solvent, which was chosen to give good separation of the monomer ($R_f=0.37$) vs. impurity ($R_f=0.07$) on analytical TLC (E. Merck). All purification were carried out in the dark so as to prevent polymerization of the monomer. The monomer obtained was checked by TLC and stored at -5°C , yield: 77%; ^1H NMR: 1.96 ppm ($-\text{CH}_3$) 5.5 and 6.1 ppm ($=\text{CH}$), 5.6 ppm ($\text{Ar}-\text{CH}_2-\text{O}$), 7.3–7.9 ppm (aromatic ring); UV: $\lambda_{\text{max}}=282$ nm.

Benzene was dried over molecular sieves for a week and then distilled. 2,2-Azobisisobutyronitrile (AIBN) was purified twice by recrystallization from methanol solution, m.p. = $106\sim 107^{\circ}\text{C}$.

Copolymerization

Copolymerization with various ratio of mixture of NMMA and MMA was carried out in benzene at 80°C under nitrogen using AIBN as initiator by 0.1% wt. The total monomer concentration was about 25 g per 100 ml benzene, and the conversion reached was generally less than 30%. After polymerization, the product was precipitated out and washed several times with fresh methanol, then dissolved, reprecipitated and washed with $\text{CHCl}_3/\text{MeOH}$ solvent system, dried in vacuo for two or three days.

Measurements

Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer using films cast on NaCl discs. ^1H NMR spectra were recorded on a Varian T-60 60 MHz spectrometer in CDCl_3 with TMS as internal reference. The molecular weight of the copolymers containing naphthalene groups was measured by GPC with the following systems: ethyl acetate, KIT 1917 (DuPont) column, Fluorometer (Krotos FS970) and RI (Waters) detector for the copolymers with lower content of NMMA; toluene, ultrastyrigel (10^4 , 10^5 Å) column, RI (Waters) and UV-VIS (Hitachi 100-40) detector for PNMMA and the copolymers with higher content of NMMA. The contents of NMMA in the copolymers were determined by Cary 14 UV-VIS spectrometer in CHCl_3 at $\lambda_{282\text{nm}}$ using PNMMA as standard. The steady state fluorescence spectra were taken on a SLM model 4800 and a Perkin-Elmer MPF 44B spectrofluorometers at $\lambda_{\text{ex}}=280$ nm.

RESULTS AND DISCUSSION

Free radical copolymerization

The data and time-conversion curves of copolymerization of NMMA with MMA are shown in Table 1 and Fig. 1, respectively. The conversion curves indicated that the process is of first order in nature, and polymerization rate increases with increasing temperature, while

Table 1 NMMA-MMA radical copolymerization in benzene at 80°C

Sample code	Copolymerization			Copolymer			
	NMMA' (mol %) in feed	Polymerization time(h)	Conversion (%)	Composition (mol %) NMMA	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	Dispersion $\bar{M}_w/\bar{M}_n$
1	0.0018	3	27.2	0.002	5.0	7.7	1.54
2	0.024	2.5	15.0	0.04	4.2	8.2	1.95
3	0.10	3.5	35.0	0.12	4.0	8.4	1.71
4	0.50	2.5	20.3	0.59	6.1	10.7	1.76
5	0.95	2.5	18.3	1.10	5.5	10.9	1.98
6	2.00	2.5	22.8	2.44	4.8	8.3	1.71
7	5.00	3.0	23.0	6.19	5.2	9.5	1.84
8	10.00	3.0	29.4	12.35	5.3	18.2	3.42
9	30.00	3.0	24.6	43.17	3.8	9.5	2.51
10	50.02	3.0	26.4	56.79	6.6	13.9	2.10
11	70.00	3.0	30.0	76.63	5.8	11.7	2.01
12	90.00	3.0	29.4	92.13	6.0	13.1	2.17
13	100.00	4.5	42.0	100.00	7.6	9.5	1.26

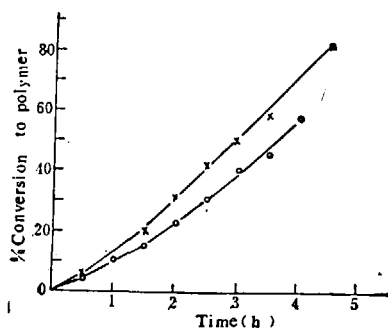


Fig. 1 The copolymerization of NMMA with MMA (mol. ratio in feed: 2/98) at 70°C (-O-) and 80°C (-x-) in the presence of AIBN

acceleration does not occur below 80°C at a higher conversion. This is to say that in the case the termination rate constant does not show a large decrease. It was found that the peak molecular weight of the copolymers did not change with conversion, as listed in Table 2.

Table 2 The relationship between conversion and peak molecular weight of the copolymers

Polymerization time (min)	30	60	90	120	150	180	210	240
Conversion (%)	4.5	9.8	15.0	22.9	30.1	40.9	45.7	57.9
Peak molecular weight $\times 10^{-4}$	6.5	7.0	6.5	6.3	6.5	6.5	6.8	7.0

The copolymers for reactivity ratio measurement were sampled when the conversion was less than 7%, and then analyzed by UV spectroscopy in CHCl_3 at maximum of $\lambda_{282\text{nm}}$. The results are summarized in Table 3. The reactivity ratio of NMMA (M_1) and MMA (M_2) were evaluated by graphical method according to Fineman-Ross plot, as given in Table 3.

Table 3 Copolymerization parameters

Sample code	Copolymerization			Composition of copolymer		Calculated parameter	
	NMMA (mol %) in feed	F	Conversion (wt %)	NMMA (mol %)	f	$\frac{F(f-1)}{f}$	$\frac{F^2}{f}$
4	0.50	199.00	6.0	0.60	165.67	197.80	239.04
7	5.00	19.00	5.1	6.32	14.82	17.72	24.35
8	0.95	9.00	7.2	11.50	7.68	7.83	10.55
9	30.00	2.33	2.5	42.53	1.35	0.60	4.02
10	50.02	1.00	5.4	49.08	1.04	0.04	0.96
11	70.00	0.43	2.3	61.72	0.62	-0.26	0.30
12	90.00	0.11	5.2	76.54	0.31	-0.25	0.04

The reactivity ratios were obtained from the slope and intercept, $r_1=0.83$, $r_2=0.89$. Because $r_1 \approx r_2$, and both of them are less than unity, it can be seen the copolymer compositions start out richer in M_1 than the feed mixture, and then cross the 45° line, and then it is richer in M_2 beyond this crossover point.

Characterization of the copolymers

So far as we know, there is no information in the literature on NMMA-MMA copolymers. Fig. 2 shows the IR spectra of PNMMA and NMMA-MMA copolymer. In comparison with the IR spectrum of PMMA, a strong C=O band at 1740 cm^{-1} was observed. For MMA unit, the characterized absorptions are C—H stretch at 3000–2800 cm^{-1} , C—H bending near 1450

cm^{-1} , C—O stretch between $1280\text{--}1150\text{ cm}^{-1}$ and CH rocking at 750 cm^{-1} . Aromatic ring of NMMA unit is readily characterized by two bands, both of which are broad and strong, at 750 and 690 cm^{-1} (out-of-plane C—H deformation of a mono-substituted aromatic group), as well as between $3100\text{--}3000\text{ cm}^{-1}$ (C—H stretching).

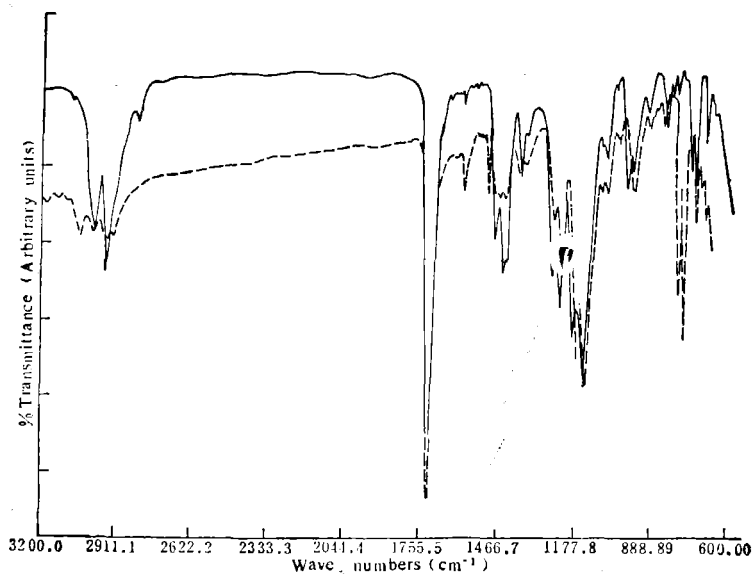


Fig. 2 The IR spectra of PNMMA (---) and NMMA-MMA copolymer (—)

Other ring mode peaks occur in the region of $1600\text{--}1575\text{ cm}^{-1}$ and $1500\text{--}1425\text{ cm}^{-1}$. It can be pointed that most of the bands of NMMA and MMA units mentioned above overlap each other. But the relative intensities of ring mode absorptions in the region of $1600\text{--}1575\text{ cm}^{-1}$ and aromatic proton bands between $3100\text{--}3000\text{ cm}^{-1}$ increase with increasing content of NMMA in the copolymers.

^1H NMR spectra of PNMMA and NMMA-MMA copolymer are shown in Fig. 3. The signal for the aromatic proton (a) is a complex multiplet spread between $7.0\text{--}8.0\text{ ppm}$. The resonances at 5.4 , 0.6 and 1.6 ppm are assigned to the protons b, c and d respectively in NMMA unit. It was also noted the intensities of the signals at $7.0\text{--}8.0\text{ ppm}$ and 5.4 ppm progressively increase with increasing content of NMMA unit in the copolymers, while the resonance at 3.6 ppm for methyl ester proton (e) in MMA unit conversely decreases.

The molecular weight and molecular weight distribution of the copolymers were measured by GPC. Monodisperse polystyrene ($MW: 4 \times 10^3 \sim 9 \times 10^5$) and PMMA ($MW: 2.7 \times 10^4 \sim 4.0 \times 10^5$) standards were first carried out to obtain the molecular weight calibration curves. The data measured could be fitted into the equation $\log MW = A - B \cdot V_r$, where V_r is retention volume of the standard samples. The slope B and intercept A were calculated to be 0.21 and 8.54 for PSt, 0.86 and 11.57 for PMMA respectively. The $\bar{M}_n$ and MWD of the polymers were then determined by GPC under the same condition. The MWD data, as listed in Table 1, were not corrected for zone spreading effect of the instrument.

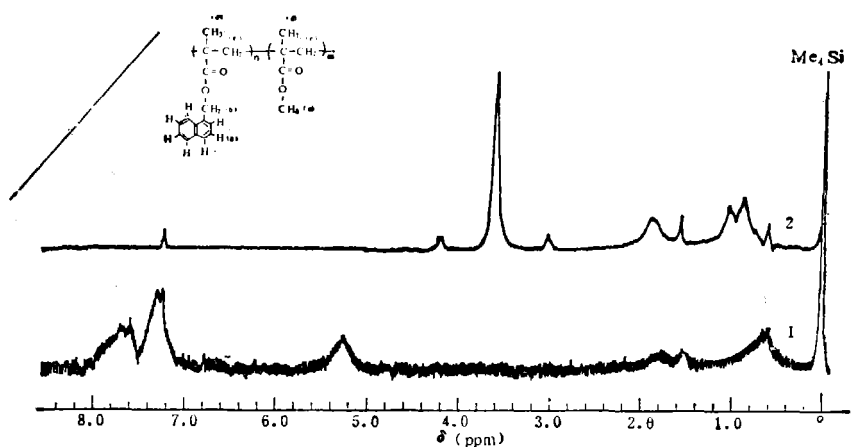


Fig. 3 60 MHz ^1H NMR spectra of PNMMA (bottom) and NMMA-MMA copolymer

PNMMA and its copolymers have the same absorption spectra with a maximum at $\lambda = 282$ nm (Fig. 4). Considering that there is a similar chemical environment for naphthalene

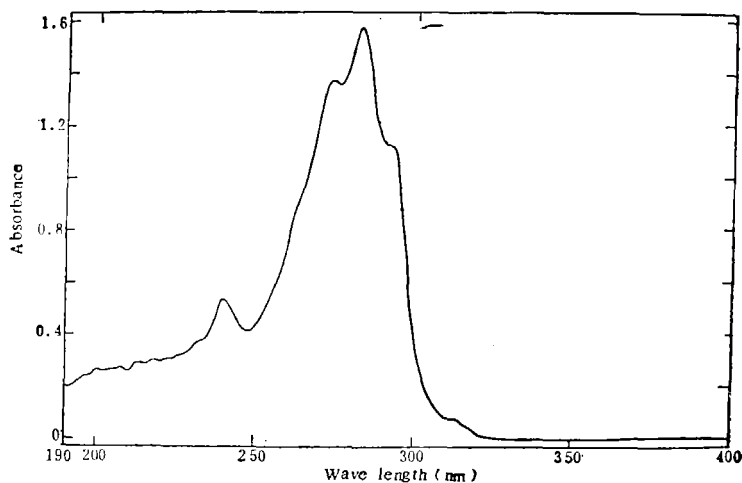


Fig. 4 UV spectrum of the polymer containing naphthalene groups, in CHCl_3

chromophores in PNMMA and its copolymers, PNMMA was used as a model compound for calculating NMMA content of the copolymers according to the equation: $A = \epsilon C$, where A , C and ϵ represent absorbance, molar concentration of NMMA and excitation coefficient, respectively. $\epsilon_{282}^{\text{CHCl}_3}$ of PNMMA was obtained to be 6524 from the slope of plotting A vs. C . The correlation coefficient of the data for PNMMA is 0.9997. To calculate NMMA content in the copolymers, the absorbances of the solutions with several concentrations for each copolymer were measured. Based on the equation:

$$\text{NMMA} = \frac{N \times M_2}{W - N(M_2 - M_1)}$$

where N , W , M_1 and M_2 are mol of NMMA in solution, sample weight per L. solution, molar weight of NMMA unit and molar weight of MMA unit respectively, NMMA content of each copolymer was calculated with deviations less than $\pm 3\%$ (Tables 1 and 4).

Table 4 UV analysis data for copolymer composition

Copolymer 3			Copolymer 7			Copolymer 12		
$C \times 10^5$ (g/ml)	A	NMMA % (mol)	$C \times 10^5$ (g/ml)	A	NMMA % (mol)	$C \times 10^5$ (g/ml)	A	NMMA % (mol)
1677.92	1.24819	0.12	49.70	1.73661	6.22	4.816	1.29689	89.16
1258.44	0.94753	0.12	34.40	1.23295	6.01	3.612	0.97914	90.30
1072.00	0.82274	0.12	24.85	0.91878	6.21	2.8896	0.79498	93.09
536.00	0.41713	0.12	20.64	0.75267	6.11	2.1672	0.59993	94.13
214.40	0.16754	0.12	15.14	0.55067	6.09	1.4448	0.40108	94.24
171.52	0.13245	0.12	12.42	0.46716	6.31	0.7224	0.19952	91.83
128.64	0.10141	0.12	6.21	0.23724	6.38			
Average		$0.12 \pm 0\%$	Average		$6.19 \pm 3\%$	Average		$92.13 \pm 3\%$

All the fluorescence spectra of the copolymer solutions with the concentration less than 10^{-4} mol (in terms of NMMA unit) shown only a monomer emission with a maximum at $\lambda = 338$ nm. Otherwise, from the fluorescence spectra of PNMMA and its copolymers, in which the NMMA contents are higher than 6% by mol, both monomer and excimer emissions

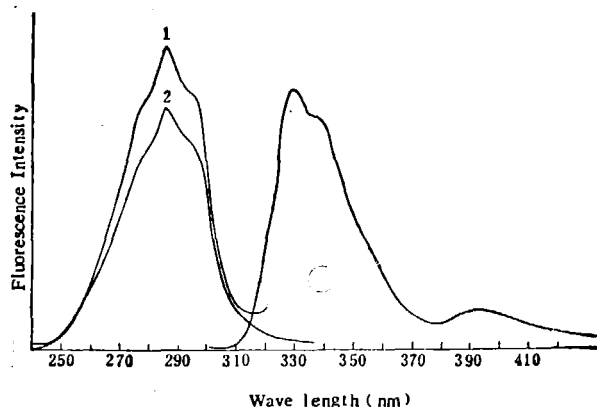


Fig. 5 Fluorescence (right) and fluorescence-excitation (left) spectra of the polymers containing naphthalene in CHCl_3 , $\lambda_{\text{ex}} = 280\text{nm}$, $\lambda_{\text{em}} = 330\text{nm}$ (1) and $\lambda_{\text{em}} = 390\text{nm}$ (2).

($\lambda=390$ nm) were observed due to the efficient intramolecular excimer formation of the naphthalene chromophores. The solid state polymers, in which the NMMA contents are even about 2% by mol, also shown excimer emission apparently due to the efficient inter- as well as intra-molecular excimer formations. Moreover, the fluorescence and absorption spectra are mirror image with each other, and their excitation spectra are similar to the absorption spectra, as shown in Fig. 5. It indicated that the origins of monomer and excimer emission are the same and the excimer emission is not from ground-state dimer formation.

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