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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Aran, Bengi and Usanmaz, Ali(2006) 'Stereoregular Polymerization of Methylmethacrylate by Atom Transfer Radical Polymerization', *Journal of Macromolecular Science, Part A*, 43: 2, 233 – 245

To link to this Article: DOI: 10.1080/10601320500437086

URL: <http://dx.doi.org/10.1080/10601320500437086>

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Stereoregular Polymerization of Methylmethacrylate by Atom Transfer Radical Polymerization

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Methyl methacrylate (MMA) was polymerized by the atom transfer radical polymerization (ATRP) method to obtain living low molecular weight polymers. The initiator was p-toluenesulfonylchloride and the catalyst ligand complex system was CuCl-4,4'-dimethyl 2,2'-bipyridine. Polymers with controlled molecular weight were obtained. The polymer chains were shown by NMR spectrum to be mostly syndiotactic. The molecular weight distributions were measured by the GPC method. The K and α constants in $[\eta] = KM^\alpha$ equation were measured as 9.13×10^{-5} and 0.74, respectively. FT-IR and X-Ray results showed stereoregularity in polymer chains. The thermal properties were studied by DSC and molecular weight-glass transition temperature relations were determined.

Keywords controlled living polymerization, ATRP, methyl methacrylate, GPC, monodispersed polymer

Introduction

Poly(methyl methacrylate), PMMA is one of the most important commercial polymers which is used as a biomaterial and in different industrial applications. Therefore, the synthesis of PMMA with the required properties is important. There are large numbers of reports on the subject, but many questions still must be answered. In many applications of polymers, the composition, molecular architecture, molecular weights and molecular weight distributions are important. Most of these have been achieved by improvements in the controlled living radical polymerization (CRP) method (1, 2). The technique used in CRP are transfer radical polymerization (ATRP), reverse addition fragmentation chain transfer process (RAFT), nitroxide mediated polymerization (NMP) and stable free radical polymerization (SFRP). The mechanism of these techniques is well documented in review articles (1, 2) and other papers (3–7). The ATRP method started in 1995 (3–5) and more than 3000 papers have been published in the last ten years. Typical monomers polymerized by the ATRP method are styrene, methacrylates, methacrylamides, acrylonitrile, acrylic acid, etc. In the ATRP method there is a dynamic equilibrium between growing radicals and large amounts of dormant species that are unable to propagate and self-terminate. In this case, the bimolecular termination is restricted and a radical

Received and Accepted June 2005.

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molecule is active (living polymer) all the time. The equilibrium parameters depend on the chosen formulation. Therefore, many papers (8–19) reported on different ATRP formulations in polymerization of methyl methacrylate, MMA.

In this study, MMA is polymerized by the ATRP method. The detailed nature of the structure of polymer obtained by ATRP has not been reported. Therefore, in this work, in addition to the kinetics of polymerization, the structure and possible stereoregularity of the polymer is investigated. The molecular weight distribution, thermal properties, and structure of polymer are studied by FTIR, NMR, DSC, GPC and X-ray.

Experimental

Materials

Methyl methacrylate (Merck), 4,4'-dimethyl 2,2'-bipyridine (Fluka), copper(I)chloride (Riedel-De-Haen), and p-toluenesulfonylchloride (Aldrich), methanol and toluene (Merck) were all reagent grade and used without further purification.

Polymerization

The reactants, 4,4'-dimethyl-2,2'-bipyridine, CuCl, p-toluene sulfonyl chloride and MMA in desired ratios were placed in a Pyrex polymerization tube and degassed at $10^{-5} - 10^{-6}$ atm for 5–6 h on the high vacuum system. The tube was sealed and placed in an oil bath at 90°C. After the desired polymerization time, the tube was immediately frozen in liquid nitrogen and opened. The contents were first dissolved in toluene, and then the polymer precipitated in excess methanol. It was dried under vacuum at 50°C to a constant weight and the conversion calculated gravimetrically.

Polymer Characterization

The molecular weight and molecular weight distributions were determined by the GPC method in THF at 25°C using Agilent HP GPC. Polystyrene ($K = 0.01363$ mL/g, $a = 0.714$ in THF at 25°C) was used as the standard. The viscosities of the polymer samples were measured at 25°C by a Ubbelohde glass viscometer using toluene as the solvent.

The NMR spectrum of monomer and polymer were taken on a Bruker Ultrashield 400 MHz Digital NMR. The FTIR spectra were taken on a Perkin-Elmer FT-IR Spectrometer using KBr pellets. The DSC thermograms of the samples were taken on a TA-DSC 910S differential scanning calorimeter with a heating rate of 10°C/min in a temperature range of -20°C–350°C under nitrogen gas atmosphere. The X-Ray powder diffraction patterns (XRD) were taken on a Rigaku Miniflex with Cu ($K\alpha$ 30 kV, 15 mA, $\lambda = 1.54178 \text{ \AA}$) radiation.

Results and Discussion

Polymerization of MMA by the ATRP Method

Methyl methacrylate, MMA was polymerized in an oil bath at 90°C by the ATRP method using CuCl/4,4'-dimethyl 2,2'-bipyridine as a catalyst system and p-toluenesulfonylchloride as the initiator in the ratios given in Table 1. First, the concentration of the

Table 1
Reactants combination used in polymerization of MMA by the ATRP method

Samples	mL of MMA	mol of ligand (10^{-5})	mol of CuCl (10^{-5})	mol of pTsCl (10^{-5})
A1	2	2.01	1.01	0.49
A2	2	2.01	1.01	0.66
A3	2	2.01	1.01	0.99
A4	2	2.01	1.01	1.99
A5	2	2.01	1.01	3.99
B1	0.5	2.01	1.01	1.99
B2	0.67	2.01	1.01	1.99
B3	1	2.01	1.01	1.99
B4	4	2.01	1.01	1.99

monomer, ligand and CuCl were held constant and the concentration of the initiator was changed for 5 runs (Athinsp; A1 to A5). Then, the concentration of the ligand, CuCl, and initiator were constant and that of the monomer was changed. For each sample group conversion at different times were measured. The polymerization reaction is highly exothermic and the heat of polymerization could not be dissipated readily from the viscous medium. The polymer samples were in the form of a white powder and soluble in solvents such as THF, toluene, chloroform, etc.

The percent conversion against polymerization time for ATRP polymerization carried out at various initiator concentrations (A1 to A5 samples) is plotted in Figure 1. The polymerization curves exhibit a two-stage propagation rate. In the first stage, the rate of polymerization is high, and the change of conversion with time is almost linear. In the second stage, the rate decreased and conversion reached a limited value, which changes with initiator concentration.

In order to have a better understanding of the change of conversion with the initiator concentration; the log (percent conversion) at 48 h polymerization time for each experimental set of A1 to A5 are plotted against the log (moles of initiator) in Figure 2 slope of the line obtained is almost zero.

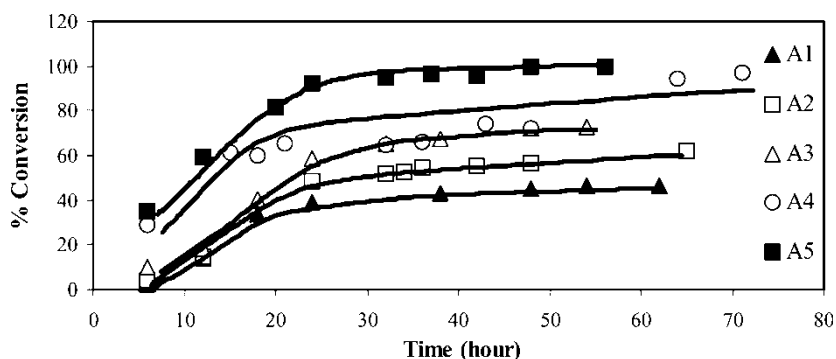


Figure 1. ATRP polymerization of MMA for different initiator concentration.

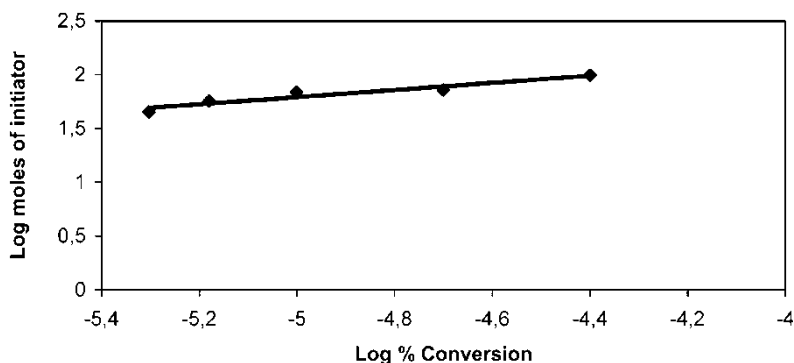


Figure 2. Percent conversion vs. number of mol of initiator in log scale.

It has been proposed that (5) the termination rate coefficients are chain length dependent and decrease during the polymerization, producing a steady rate of polymerization. This helps to form well-defined polymers at higher conversions. However, when the monomer concentration becomes very low, propagation slows down but termination and other side reactions may still occur with the usual rate. Thus, there is a certain window of concentration and conversions where the polymerization is well controlled. In the last five sets (A4 and B1 to B4), the amounts of the ligand, CuCl, and initiator were constant, and that of the monomer changed. The percent conversions vs. time plot for these sets of samples are shown in Figure 3. The reaction rate is higher for the samples that have lower monomer concentrations. This shows that there should be an optimum range for the ratio of monomer to initiator concentration. At the given concentration of initiator, the rate of reaction decreased with the increase of monomer concentration. In order to have a better understanding for the change of conversion with monomer concentration,

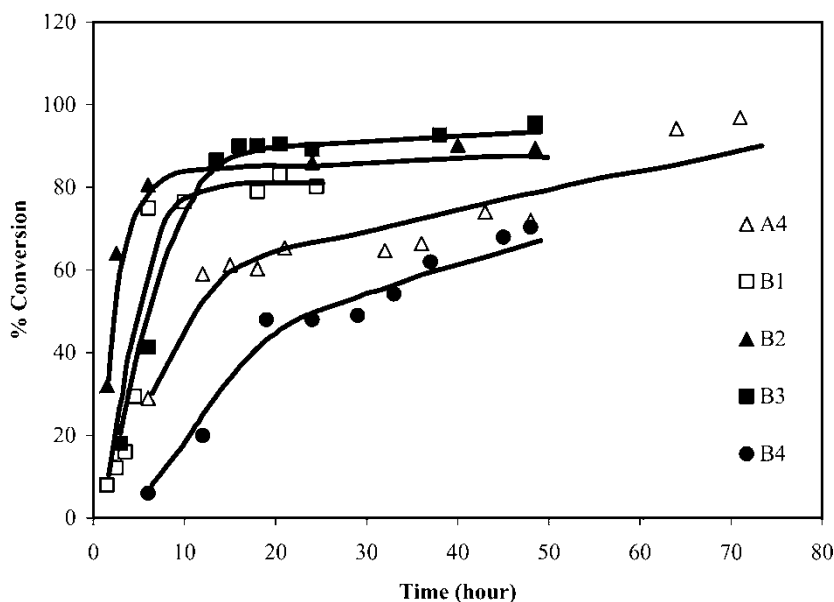


Figure 3. ATRP polymerization of MMA for different monomer concentration.

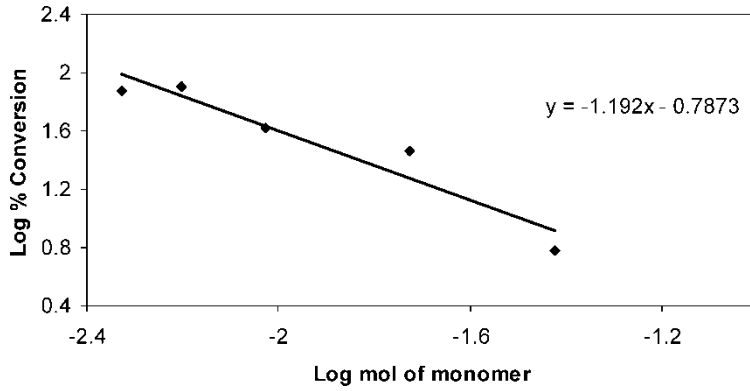


Figure 4. Percent conversion vs. number of mol of monomer in log scale.

the log (percent conversion) at 6 h polymerization time for each experimental set of A4 and B1–4 are plotted against log (moles of monomer) in Figure 4. The percent conversion decreased almost linearly with monomer concentration. Thus, the reaction order with respect to monomer concentration will not give a meaningful value at the studied initiator concentration.

FTIR Investigation

The FT-IR spectra obtained for MMA and PMMA are shown in Figure 5. In the IR spectrum of monomer (Figure 5a) the peak assignments are as follows: a characteristic carbonyl

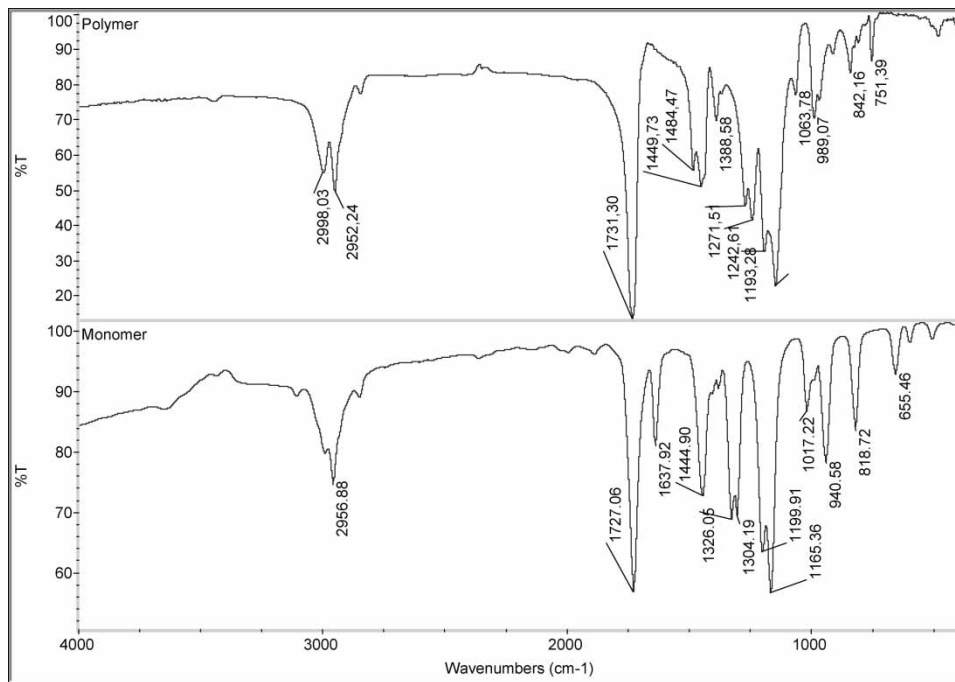


Figure 5. FTIR spectra of MMA and PMMA.

stretch of the ester at 1727 cm^{-1} ; the $\text{C}=\text{C}$ at 1638 cm^{-1} and at 940 cm^{-1} ; the CH_2 at 1444 cm^{-1} ; the $(-\text{O}-\text{C}-)$ stretching at 1199 cm^{-1} ; the $-\text{O}-\text{CH}_3$ at 2956 cm^{-1} and the CH_3- at 1326 cm^{-1} . In the spectrum of PMMA (Figure 5(b)), the carbonyl stretch of the ester at 1731 cm^{-1} retained its position, but that of $\text{C}=\text{C}$ at 1638 and 940 disappeared. The peaks at $1272-1147\text{ cm}^{-1}$ correspond to $\text{C}-\text{C}-\text{O}$, $\text{O}-\text{C}-\text{C}$ and $\text{C}-\text{C}-\text{C}$ stretching vibrations. The peak at 989 cm^{-1} to the end group $\text{C}=\text{C}$, which also shows that the termination of PMMA is mostly by disproportionation and also chains are in syndiotactic configuration. The sharpness of FT-IR peaks in polymer spectrum is also evidence of the stereoregularity of polymer chains.

It can be concluded from the IR spectra investigation that the polymer was successfully achieved and the polymerization proceeds by carbon-carbon double bond opening. The spectra of polymer samples obtained in this work were all identical to that in Figure 5(b).

NMR Investigation

The $^1\text{H-NMR}$ spectrum of methyl methacrylate monomer is given in Figure 6. There are four peaks at 1.79 (H_c), 3.62 (H_d), 5.43 (H_a), and 5.97 (H_b) ppm. The assigned protons and their peaks are given in Figure 6.

In the $^1\text{H-NMR}$ spectrum of PMMA (Figure 7), the signals at 0.59–0.95, 1.17–1.77, and 3.14–3.48 ppm are assigned to the protons of methyl groups [peak a] of $-\text{C}(\text{CH}_3)$ (COOCH_3), methylene groups [peak b] of $-\text{CH}_2-$, and methoxy groups [peak c] $-\text{C}(\text{CH}_3)$ (COOCH_3), respectively. The peak at 3.48 ppm [peak c(ω)] is for the protons of the methoxy group, that at 2.08 ppm [peak b(ω)] is for the methylene protons, and that at 0.95 ppm [peak a(ω)] exhibits the characteristic chemical shifts of the terminal MMA unit capped with an ω -end chlorine. The assigned peaks explain that the polymers have a predominantly syndiotactic structure (20). Similar spectra were also observed for polymers obtained under different conditions. Thus, the end group analysis by $^1\text{H-NMR}$ gives information for the mechanism of ATRP.

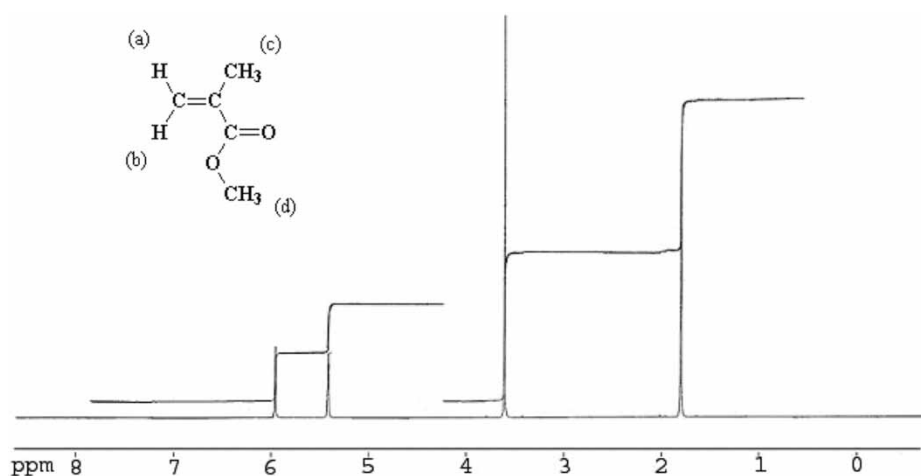


Figure 6. $^1\text{H-NMR}$ spectrum of monomer (MMA).

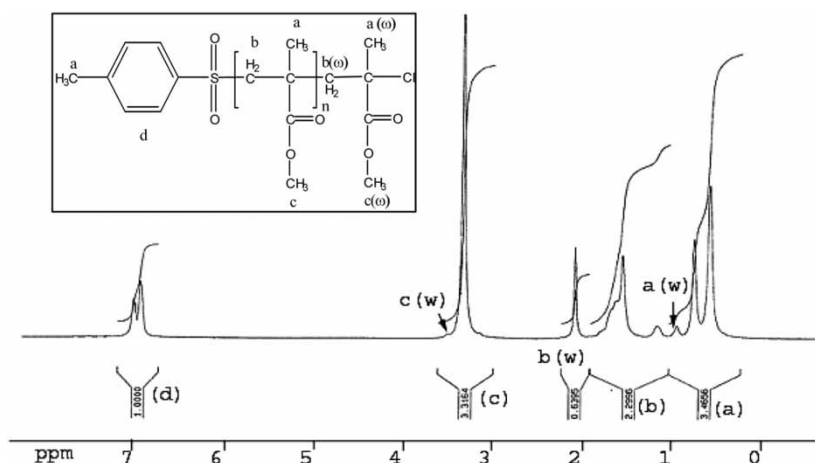


Figure 7. ^1H NMR spectrum of polymer (PMMA).

Molecular Weight Determination

The molecular weight of polymers was determined by GPC and viscosity methods. The GPC molecular weight distribution curves for the polymer samples of some A4 sets are given in Figure 8 and the results are tabulated in Table 2. The molecular weights show normal distribution in a narrow range. The dispersivity constant changes between 1.99 to 3.28, and increases with polymerization time. The molecular weights generally increased with polymerization time. Thus, monodispersed polymers can be obtained at lower conversions and lower molecular weights.

Mark-Houwink equation;

$$[\eta] = KM^\alpha$$

$$\log[\eta] = \alpha \log M_w + \log K$$

The plot of $\log[\eta]$ against $\log M_w$ (Figure 9) gives a straight line with intercept $\log K$ and slope α . Mark-Houwink coefficients, K (9.13×10^{-5}) and α (0.74) were found from the intercept and the slope of the straight line obtained when viscosities were measured in toluene at 25°C . The equation becomes:

$$[\eta] = 9.15 \times 10^5 M^{0.74} (\text{viscosities in toluene at } 25^\circ\text{C})$$

The viscosity average molecular weights for other polymer samples calculated using the given relation is given in Table 3. Molecular weight increased with polymerization time for all sets of samples. The increase in the concentration of the initiator or/and monomer does not show a regular trend, but the molecular weight and molecular weight distribution can be controlled by proper ratio of monomer and initiator.

DSC Investigation

Differential scanning calorimeter is one of the most widely used techniques to measure T_g and T_m . The measurements were carried out at N_2 atmosphere by heating polymer samples in the temperature range of -25°C – 300°C . The DSC thermograms of polymer

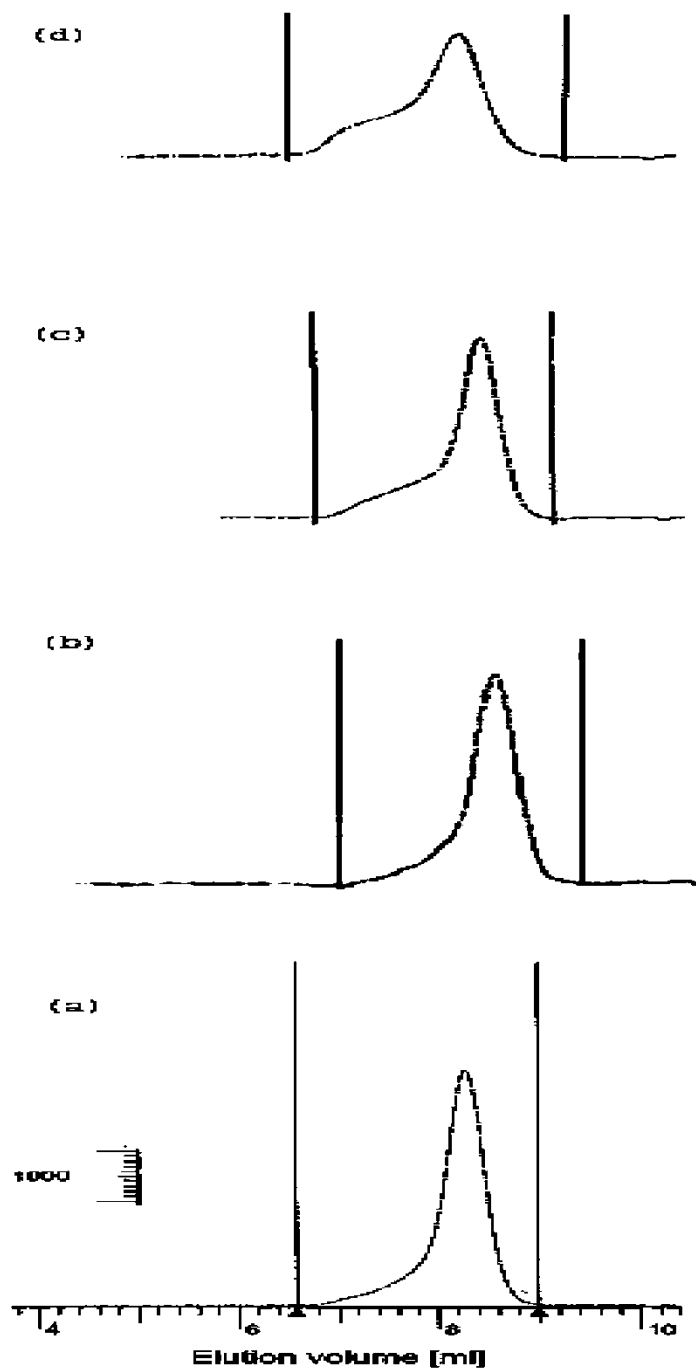


Figure 8. GPC curves of samples A4 (polymerization time: a: 12; b: 15; c: 18; and d: 21 h, respectively).

Table 2
GPC results with polystyrene ($K = 0.01363 \text{ mL/g}$, $a = 0.714$ in THF at 25°C) as the standard

A4 time hour	$M_w 10^{-4}$ (g/mol)	$M_z 10^{-5}$ (g/mol)	$M_v 10^{-4}$ (g/mol)	$M_n 10^{-4}$ (g/mol)	$M_p 10^{-4}$ (g/mol)	D	$[\eta] 10^{-1}$ (mL/g)
12	10.878	2.433	9.637	5.453	5.544	1.99	4.932
15	7.506	2.262	6.324	3.044	3.174	2.46	3.651
18	13.930	3.130	12.068	5.615	5.080	2.48	5.791
21	18.363	3.573	16.081	5.590	6.606	3.28	7.109

samples are given in Figures 10 and 11. In the thermograms of some samples, the multiple melting peaks are observed showing the existence of a low percentage of poly crystalline fraction. The T_g of polymer samples and molecular weights are tabulated in Table 4.

The plot of T_g against $1/M_n$ for Fox-Flory equation is given in Figure 12. The T_g 423 and $K(4.3 \times 10^{-3})$ values were found from the intercept and slope of the straight line obtained thus, for PMMA:

$$T_g = 423 - \frac{4.3 \times 10^{-3}}{M_n}$$

The T_g value of 423 K might seem larger than the usually accepted value of 382 K. However, similar values are reported for highly crosslinked PMMA from DMA studies (21) which is more sensitive to molecular vibrations.

X-Ray Investigation

The X-Ray powder pattern of PMMA sample is given in Figure 13. The samples could not be powdered properly and therefore, particulate sizes were large. This will affect the X-Ray powder pattern to give information about the chain orientations, but not detailed

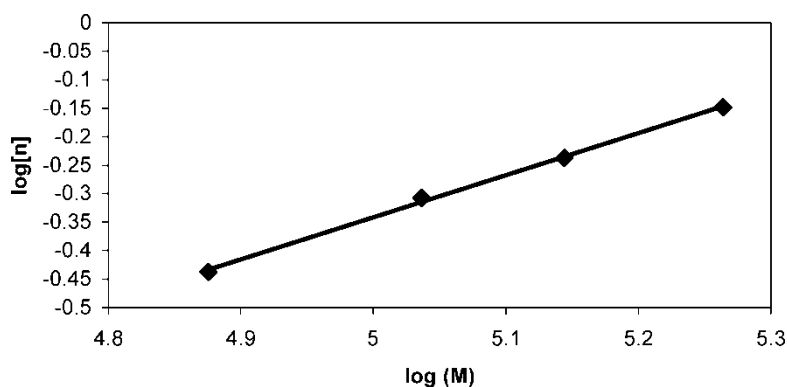


Figure 9. Log plot of $[\eta]$ vs. M_w for PMMA with viscosities in toluene at 25°C .

Table 3
The percent conversion vs. molecular weight for the sets

	% Conv.	Mv (g/mol)
A1	10	24889
	18	32304
	58.4	86665
	72.9	107157
A2	61.2	50376
	60.3	78018
	74	98854
	96.9	224545
A3	94.9	19714
	96.2	26968
	95.6	34345
	99.6	43727
A4	33.6	70799
	39	86068
	45	118430
	46.8	165020
A5	15	55837
	48.8	44037
	52.5	162503
	56.7	236247
B1	16	12497
	75	25989
	79	84453
	80.2	247320
B2	32	33921
	64	43299
	80.6	72125
	89.4	247582
B3	18	53615
	86.6	108231
	90.6	155903
	95.6	249977
B4	20	10315
	48	11141
	48.95	12428
	54.23	14264

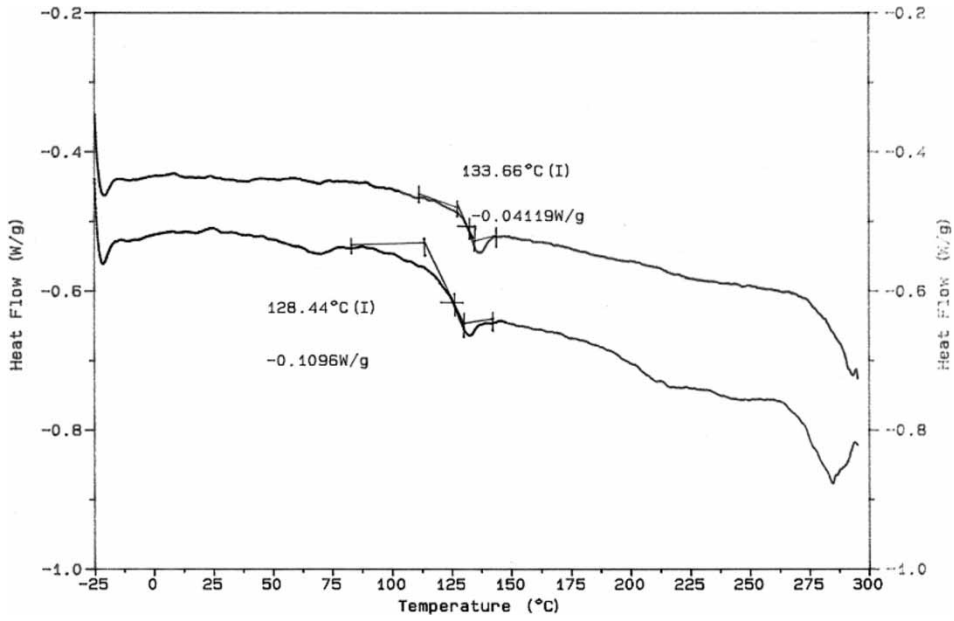


Figure 10. DSC thermograms of samples B2/24 and B2/48.5.

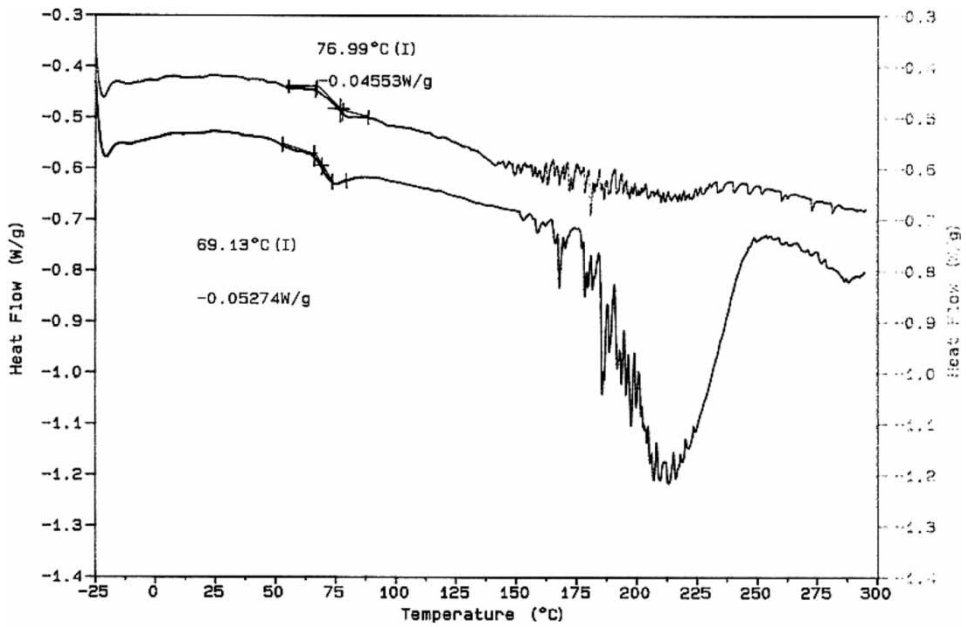


Figure 11. DSC thermograms of samples of A5/12 and B4/19.

Table 4
 T_g values of PMMA from Figure 10

Sample/time(h)	T_g (K)	MW(g/mol)
B2/24	407	28869
B2/48.5	402	18112
A5/12	350	5894
B4/19	342	5241

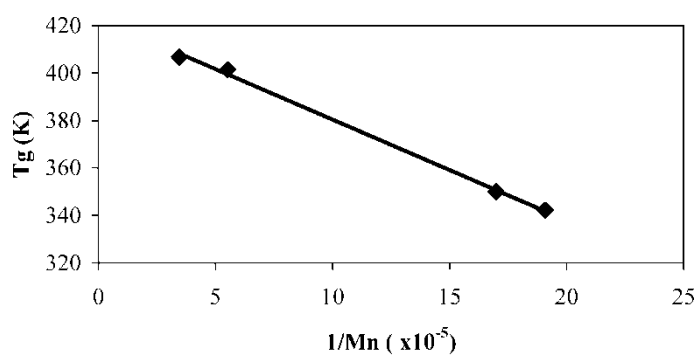


Figure 12. Glass transition temperature vs. reciprocal M_n for PMMA.

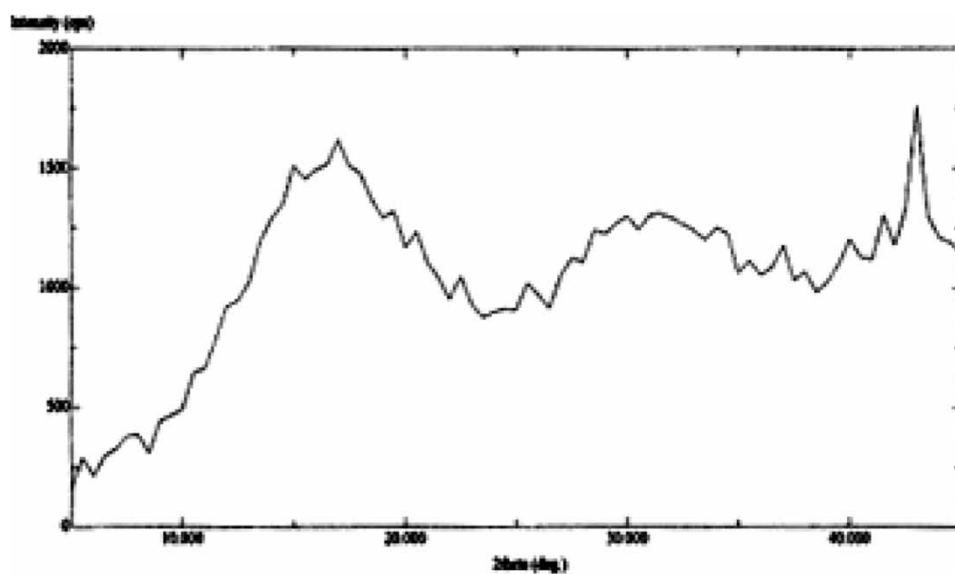


Figure 13. X-Ray spectrum of set 9/time 48 (hour).

characteristic X-Ray peak of the sample. Thus, in Figure 13, the broad peaks show orientation and chain structure regularity. The percent crystallinity is not large.

Conclusions

Methyl methacrylate was polymerized by the ATRP method to give syndiotactic polymer with a low degree of crystallinity. The FTIR and NMR results were used to determine the structural nature of the polymer. The results give a possible mechanism of the polymer process. The molecular weight distribution was shown by GPC measurements. The K and α values for molecular weight-viscosity relation was found. The change of glass transition temperature with molecular weight was shown by DSC results.

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