

THE EFFECTS OF MAGNETIC FIELD ON GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ONTO POLYVINYL ALCOHOL IN THE PRESENCE OF BENZOPHENONE DURING UV IRRADIATION

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ABSTRACT

The effects of magnetic field on the graft ratio and stereoregularity of grafts of PVA-g-MMA in the presence of benzophenone during UV irradiation are discussed. By means of IR, it was found that the graft ratio was increased with the increment of magnetic field strength. Furthermore, application of relative weak magnetic field of 0.4 Tesla had been shown to substantially enhance the stereo-regularity of graft copolymer. The maximum stereo-regularity appeared when the graft ratio approached to 85% with the magnetic field of 1.2 Tesla (T). The resistance to moisture and heat resistance of the grafted copolymer in the presence of magnetic field were also improved.

INTRODUCTION

As we know that the magnetic field can exert great influence on chemical reactions^[1] as light, pressure and heat did. It was reported that the molecular weight (*MW*) of styrene emulsion polymerization using dibenzal ketone as photochemical initiator^[2], the photocrosslinking of polyolefin^[3], the curing of epoxy resins^[4], the rate of polymerization and ordering of liquid crystalline and semicrystalline polymers^[5] were effected by magnetic field.

The graft copolymerization of MMA on PVA was carried out by us in the presence of benzophenone under UV irradiation in order to improve the PVA's resistance to moisture and optical properties. Since this grafting was a radical reaction, it was natural for us to try what should be happened if the magnetic field was applied in this system.

In the further researches, we revealed that the graft ratio of MMA onto PVA was raised with the increment of magnetic field, furthermore, application of relative weak magnetic field of 0.4 T had been shown to substantially enhance the stereo-regularity of graft copolymer. The probability found in longer sequences which were composed of more than ten successive syndiotactic MMA structure units with magnetic field was twice as much as the probability without magnetic field.

The copolymer of PVA-g-MMA formed under the influence of magnetic field had better properties than the copolymer formed without magnetic field, the glass transition temperature was about 20 °C higher than that of the latter.

EXPERIMENTAL

1. Materials

The concentration of PVA ($\overline{DP}_n = 1750$, 88% hydrolyzed) aqueous solution is about 1 ~ 3%.

MMA is purified by standard method.

2. Graft copolymerization

In a quartz tube a mixture of 0.3mg benzophenone, 2ml MMA and 10ml 3% PVA aqueous solution was stirred 15min by supersonic waves in an ice water bath, then thawed with nitrogen, sealed under vacuum and placed into the gap between two poles of electromagnet, its maximal magnetic field strength was 1.2T when the distance between two poles was 2.5cm and electric volt 220V. The tube was irradiated with 500W high pressure Hg lamp (from Shanghai Ya Ming Lamp Factory, GGZ-500) at 30 °C. At the end of the reaction, the graft copolymer was precipitated out by acetone and dried, then refluxed in acetone to remove homopolymer PMMA. The graft copolymer was dried in vacuo to constant weight.

3. Measurement

The graft ratio was evaluated according to the increment of PVA weight before and after grafting.

$$\text{Graft ratio (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

(W_1 : PVA weight before grafting, W_2 : PVA weight after grafting)

The syndiotactic and isotactic contents in the grafted PMMA were determined by the method as references^[6-7] reported.

IR spectra were recorded with Perkin-Elmer 983G spectrophotometer; (polymer sample were pressed into sheet in heating conditions) TGA and DSC were scanned with Du pont 1090B thermometer.

RESULTS AND DISCUSSION

1. The effects of magnetic field on the graft ratio and stereo regularity of graft copolymer

Table 1 shows the graft ratio of MMA onto PVA which was varied with the magnetic field strength. In the same conditions the graft ratio with magnetic field strength of 1.2T was double-fold that without magnetic field at 30 °C, but the graft ratio dropped with the enhancement of reaction temperature because the homopolymerization rate of MMA also increased with the increase of reaction temperature no matter whether in the presence or absence of magnetic field.

The IR spectra of the copolymer grafted with the condition of magnetic field or without were shown in Fig. 1. Using D1063/D1393^[6] and D749/D755 in IR spectrum of PMMA as a relative measurement of syndiotactic and isotactic contents in PMMA grafting chains. (1063: carbon-hydrogen deformation bands of C-CH₃; 1393:

symmetric carbon-hydrogen bending bands of $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OCH}_3 \end{array}$; 749, 755; CH₂

rocking absorption bands which are split when observed in solid state.) From Fig. 1b and Fig. 2, it can be seen that the syndiotactic contents in PMMA increased with the magnetic field strength of reaction conditions. Furthermore, application of relative

weak magnetic field of 0.4T has shown that it will enhance the syndiotactic contents in the grafted chains.

Table 1 The effect of magnetic field (M.F.) on the graft ratio

M. F. Strength (Tesla)	Sample No.	Reaction temp. (°C)	Reaction time (min)	W1 (mg)	W2 (mg)	W2 - W1 (mg)	Graft ratio (%)	T_g (°C)
0	1	-10	30	300.12	395.26	95.14	31.7	
	2		60	300.08	493.63	193.55	64.5	
	3		100	300.26	646.16	345.90	115.2	
	4		150	300.17	760.64	460.47	153.3	
	1	30	30	300.10	358.02	57.92	19.3	
	2		60	300.32	402.73	102.41	34.1	
	3		100	300.25	443.17	142.92	47.6	
	4		150	300.19	482.71	182.52	60.8	
0.4	1	-10	30	300.06	434.49	134.43	44.8	
	2		60	300.22	553.91	253.69	84.5	
	3		100	300.18	757.69	457.47	152.4	
	4		150	300.37	835.63	535.26	178.2	
	1	30	30	300.26	419.46	119.20	39.7	
	2		60	300.11	472.37	172.26	57.4	
	3		100	300.04	688.89	388.85	129.6	
	4		150	300.17	773.84	473.67	157.8	
1.2	1	-10	30	300.38	472.50	172.12	57.3	
	2		60	300.30	558.86	258.56	86.1	
	3		100	300.23	784.20	483.97	161.2	
	4		150	300.00	850.20	550.20	183.4	
	1	30	30	300.16	452.34	152.18	50.7	
	2		60	300.15	504.85	204.70	68.2	
	3		100	300.38	708.90	408.52	136.0	
	4		150	300.09	806.94	506.85	168.9	

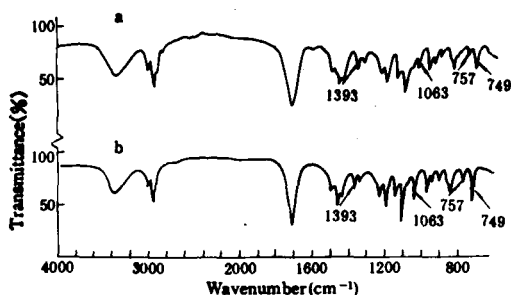


Fig.1 IR spectra of PVA-g-MMA grafted at the reaction condition with and without magnetic field. (reaction time : 30min)

a . No magnetic field, b. Magnetic field of 0.4T

In Fig. 2, it could be seen that the syndiotactic contents after reaction time of 60min became lower but rose again after 80min. The reason is that: in the graft system, the propagation reaction was carried out in the PVA micelle containing MMA monomers and benzophenone molecules. At the first period of the graft polymerization, the stereoregularity of PMMA graft chain was risen with the

increment of the strength of magnetic field and consumption of benzophenone in the micelle. There was an equilibrium between the concentrations in micelle and in water (including dissolved and undissolved benzophenone). When the equilibrium was disrupted after some time, the benzophenone in water phase might diffuse into the micelle, but at this time, it was found that the variation of stereoregularity of PMMA graft chains was less than the variation at the first period of graft polymerization. Fig. 2 shows that the variation of stereoregularity of PMMA graft chains was a process of gradual change. Having diffused into the PVA micelle, benzophenone molecules of the second batch grasped the hydrogen atom from PVA as the first batch did, then macromolecule radical PVA, initiated MMA to polymerize, but at the beginning of graft polymerization caused by the second batch benzophenone, the stereo-regularity of PMMA graft chain was more than that formed by the first batch benzophenone, so the average stereo-regularity decreased. When the reaction time increased further, the syndiotactic contents rose again because the effect of magnetic field on stereoregularity of graft copolymer with much lower graft ratio is more than with higher graft ratio as Fig. 2 shows.

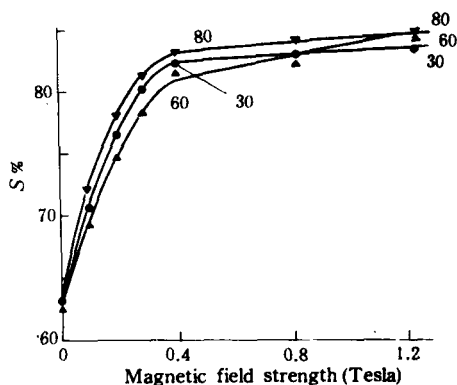


Fig.2 The effect of external magnetic field on syndiotactic contents in PMMA
(Reaction temp.: 30 °C)
Reaction time (min): ● 30, ▲ 60, ▼ 80

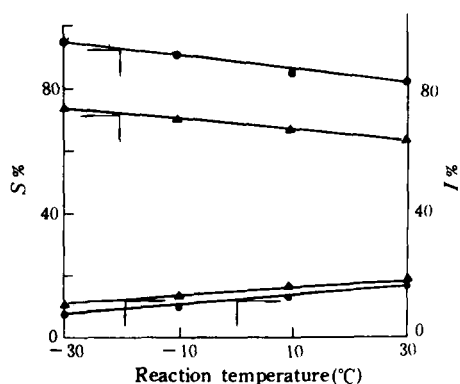


Fig.3 The effect of temperature on the stereoregularity of the sample formed with and without magnetic field. (reaction time : 30min)
● Magnetic field, ▲ No magnetic field

Fig. 3 shows that with the increase of temperature the syndiotactic contents dropped, at the same time the isotactic and heterotactic contents increased. It is in line with the regular patterns of radical polymerization.

According to the formulae^[9]:

$$f_N = \beta^{N+1} \{ 1 + (1 - \beta)N \} \quad (2)$$

$$\beta^2 = S/100 \quad (3)$$

where N : number of successive syndiotactic structure units, f_N : probability of constitution of N successive syndiotactic structure units, S : syndiotactic contents, β : square root of contents of syndiotactic structure units in PMMA.

The probability of constitution of N successive syndiotactic structure units could be calculated as Table 2 shows. This table indicates that when the reaction time is more than 30min, the contents of syndiotactic structure units in PMMA are approximately equal, no notable variation of probability of constituting the successive

syndiotactic structure could be found no matter with the presence or absence of magnetic field.

Table 2 The effect of magnetic field on the stereo regularity of PMMA segments*

M. F. Strength (Tesla)	Sample No.	Reaction time (min.)	Graft percent (%)	$\frac{D749}{D757}$	I% **	$\frac{D1063}{D1393}$	S% ***	β	f_N				
									f_5	f_{10}	f_{15}	f_{20}	f_{25}
0	1	30	19.3	2.0511	17.7	0.6584	63.5	0.7969	0.52	0.25	0.11	0.04	0.02
	2	60	34.1	2.0223	17.6	0.6553	63.3	0.7956	0.51	0.25	0.10	0.04	0.02
	3	80	41.4	2.0189	18.0	0.6533	63.0	0.7937	0.51	0.24	0.10	0.04	0.02
	4	100	47.2	2.0017	18.9	0.6507	62.1	0.7880	0.49	0.23	0.09	0.04	0.01
	5	150	60.8	1.9861	19.7	0.6495	61.9	0.7867	0.49	0.22	0.09	0.03	0.01
0.4	1	30	39.7	2.2017	16.5	1.0288	82.5	0.9105	0.82	0.68	0.52	0.39	0.28
	2	60	57.4	2.2001	16.6	1.0146	82.0	0.9055	0.81	0.65	0.49	0.36	0.25
	3	80	84.3	2.2102	15.9	1.0343	83.6	0.9143	0.83	0.69	0.55	0.41	0.31
	4	100	129.6	2.1695	17.1	1.0217	81.4	0.9022	0.80	0.64	0.48	0.34	0.24
	5	150	157.8	2.1116	17.6	1.0196	81.1	0.9006	0.80	0.63	0.47	0.33	0.23
1.2	1	30	50.7	2.3456	14.9	1.0976	83.0	0.9110	0.83	0.68	0.53	0.39	0.29
	2	60	85.2	2.3568	13.7	1.1223	84.4	0.9187	0.85	0.71	0.57	0.44	0.33
	3	80	118.4	2.2927	15.2	1.0913	82.6	0.9088	0.82	0.67	0.51	0.38	0.27
	4	100	136.0	2.2514	16.6	1.1001	82.1	0.9061	0.81	0.66	0.50	0.36	0.26
	5	150	168.9	2.2701	16.0	1.0982	81.9	0.9050	0.81	0.65	0.49	0.36	0.25

* Reaction temp.: 30 °C

** I: isotactic, *** S: syndiotactic.

Nevertheless the marked difference could be observed from the stereo regularity of the copolymer grafted with and without magnetic field. For example, when the magnetic field strength is 0 T, PMMA is predominantly syndiotactic structure, its contents are about 62%, but it is composed of short racemic sequence of no more than five MMA monomers or four dyads, the probability of forming five successive syndiotactic structure units is less than 0.52 (reaction time: 100min). When the magnetic field strength increased to 1.2 T and reaction time was 30min, the graft ratio was approximately equal to the former (reaction time: 100min, magnetic field strength: 0 T) in this case, but the probability of forming five successive syndiotactic structure units increased to 0.83.

Therefore the effect of magnetic field on the stereo-regularity in this case resulted the increase of the probability forming the long racemic sequence.

2. The relationship between graft ratio and regularity of PMMA segments

As we just mentioned, marked change of stereo-regularity of PMMA could be found only in the lower graft ratio and relatively weak magnetic field.

It is well known that the PVA is widely used as a water soluble polymer, so the graft copolymerization of MMA onto PVA is very similar to the emulsion polymerization using water as a dispersion medium.

Before the start of the grafting, the micelle containing MMA monomers and benzophenone are formed by PVA macromolecules arranged on the interface, the hydrophobic parts, namely the carbon chains of PVA faced to oil phase. As soon as the system is irradiated by UV light, the benzophenone molecules absorbed the photons transited to excited triplet state through intersystem crossing, then grasped the hydrogen

atom from the tertiary carbon of PVA and produced triplet radical pair consisted of ketyl and PVA. In the micelle, these two radicals may return to singlet state by $S \longleftrightarrow T_0$ because the triplet states (T_- , T_0 , T_+) and singlet state are degeneracy in energy due to superfine interaction between unpaired electron in radicals and nuclei spin in the absence of magnetic field. When the external magnetic field is applied on, the degeneracy is lifted by Zeeman effect produced by interaction between external magnetic field and unpaired electrons in radicals, only $S \longleftrightarrow T_0$ transition is allowed. Thus in the presence of magnetic field the number of triplet pairs increased about $2/3$ than that in its absence. These triplet pairs have longer life, are more difficult to recombine and have enough time to contact with MMA monomers to make latter polymerize, so the graft ratio of copolymer formed by triplet PVA· is higher than the graft ratio by singlet one.

When the segment size of MMA grafted on the PVA was less than or approached to the PVA macromolecules size, the graft mode was restricted by PVA cage and external magnetic field, so the stereo-regularity of PMMA onto PVA was changed with the variation of magnetic field strength. When the size of PMMA is big enough, the solubilizing effect of PVA became less and less, and PMMA segments could not be wrapped up by PVA macromolecules because there was not free PVA macromolecule reservoir in this system as that of emulsion polymerization to supply the detergent molecules for growing micelle. After that the propagation of MMA has the characteristics of solution polymerization, so no effect of magnetic field could be found^[10].

4. Improvement of the properties of resistance to moisture and heat resistance of graft copolymer with magnetic field

The thermal properties of graft copolymer of PVA-g-MMA with and without magnetic field are indicated by Fig.4 and Fig.5. Under the influence of magnetic field,

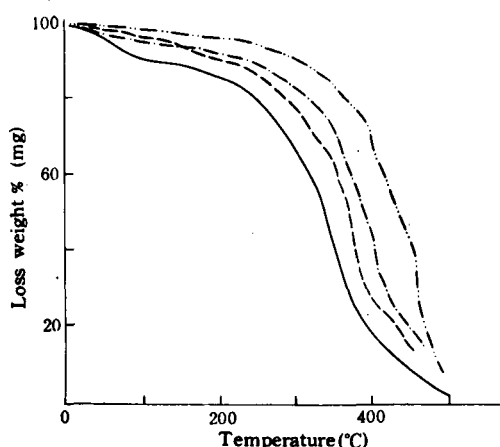


Fig.4 TGA analysis of PVA-g-MMA with and without magnetic field

- No magnetic field, graft ratio: 20.7%
- No magnetic field, graft ratio: 127.9%
- - - Magnetic field strength: 0.4T, graft ratio: 339.7%
- · - Magnetic field strength: 1.2T, graft ratio: 118%

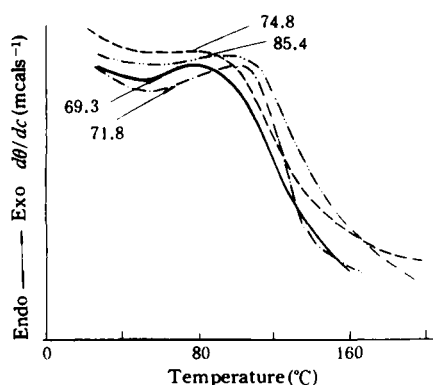


Fig.5 DSC analysis of PVA-g-MMA with and without magnetic field.

- No magnetic field, graft ratio: 19.3%
- No magnetic field, graft ratio: 127.9%
- - - Magnetic field strength: 0.4T, graft ratio: 39.7%
- · - Magnetic field strength: 1.2T, graft ratio: 118%

the initial and final decomposition temperature and the glass transition temperature (T_g) are enhanced. From Fig.4, it is seen that the TGA curves in lower graft ratio and in the absence of magnetic field show inflexions between 98 ~ 145 °C due to absorbed moisture. In the TGA curves of PVA-g-MMA formed with the reaction condition of presence of magnetic field, no inflexions were observed. This indicates that the grafted PVA is resistant to moisture absorption.

It is valuable to point out that the effect of magnetic field on graft copolymerization of MMA onto PVA is complex. The variation of T_g of graft copolymer mainly relies on the stereo-regularity when the graft ratio is less than 85%.

When the graft ratio is higher than 85%, the variation of stereo-regularity approaches to constant, the T_g of graft copolymer are mainly dependent on the graft ratio.

Keywords:

Magnetic field; Graft copolymerization; Methyl methacrylate; Polyvinyl alcohol; Benzophenone; UV irradiation

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REFERENCES

- [1] Yoshio, S.; Masayuki, Y.; Hirochika, S. and Kasumi, T., *Kagaku no Ryoiki*, **1982**, 36 (4), 259.
- [2] Turro, N. J.; Chow, M. F.; Chung, C. J. and Tong, C. H., *J. Am. Chem. Soc.*, **1983**, 105, 1572.
- [3] Martl, M. G.; Pongratz, Th. and Humme, K., *Makromol. Chem. Rapid Commun.*, **1983**, 4, 649.
- [4] Vavilov, N. I. and Loginova, A., *Mekh. Kompoz. Mater.*, **1983**, 3, 544.
- [5] Gray, M. E. and Harrison, I. R., *J. Appl. Polym. Sci.*, **1983**, 28, 3603.
- [6] Bovey, E. A. and Tiers, G. V. D., *J. Polym. Sci.*, **1960**, 44, 173.
- [7] Baumann, U., Schreiber, H. and Tessmar, K., *Makromol. Chem.*, **1960**, 36, 81.
- [8] Watanabe, H., *Kogyo Kagaku Zasshi* **1961**, 64 (10), 159.
- [9] Watanabe, H.; Kato, Y. and Nishioka, *Kogyo Kagaku Zasshi*, **1962**, 65 (2), 128.
- [10] Turro, N. J., Pierola, I. and Chung, C. J., *J. Polym. Sci., Polym. Chem. Ed.*, **1983**, 21, 1085.