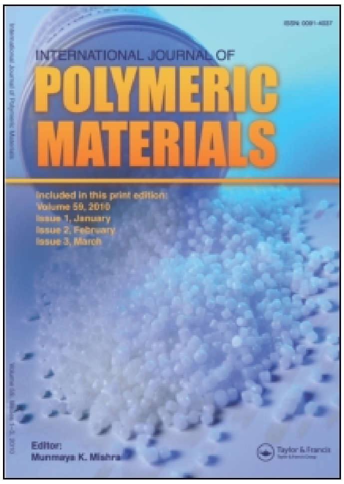

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

THE INFLUENCE OF PROCESS VARIABLES ON THE MOLECULAR MASS OF AN/MA COPOLYMERS-II

R. D. Sanderson[a]; E. R. Sadiku[a]
[a] UNESCO Associated Centre for Macromolecules and Materials, Department of Chemistry, Matieland, Republic of South Africa

To cite this Article Sanderson, R. D. and Sadiku, E. R.(2004) 'THE INFLUENCE OF PROCESS VARIABLES ON THE MOLECULAR MASS OF AN/MA COPOLYMERS-II', International Journal of Polymeric Materials, 53: 3, 249 — 260

To link to this Article: DOI: 10.1080/00914030490277752

URL: http://dx.doi.org/10.1080/00914030490277752

International Journal of Polymeric Materials, 53:249–260, 2004
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490277752

THE INFLUENCE OF PROCESS VARIABLES ON THE MOLECULAR MASS OF AN/MA COPOLYMERS-II

R. D. Sanderson and E. R. Sadiku
UNESCO Associated Centre for Macromolecules and Materials,
Department of Chemistry, University of Stellenbosch, Matieland,
Republic of South Africa

Viscometry experiments were carried out on a range of laboratory-synthesized polyacrylonitrile precursors that were to be used for the manufacture of PAN/MA hollow-fiber carbon membranes. This was done to determine the effect of the polymerization process variables on the average molecular mass of copolymers of methylacrylate and acrylonitrile. Factors such as the concentrations of methylacrylate monomer (MA) and azo-bis-isobutyronitrile initiator (AIBN), stirrer speed and polymerization temperature were investigated as functions of the molecular mass. An empirical approach that employed statistical experimental designs, used to recognize analytical and statistical methods that translate the process responses into comprehensible terms was used. It was established that hollow-fiber carbon membranes can be reproducibly prepared if the polymerization conditions are controlled. Process variables such as stirrer speed, polymerization temperature, methylacrylate and azo-bis-isobutylonitrile concentrations influence the properties of the copolymer produced and hence the properties of the carbon membranes produced from precursors made from the copolymer. The highest molecular mass PAN was obtained when the concentrations of MA and AIBN were high, while a reduced polymerization temperature favored the synthesis of high molecular mass PAN. The stirrer speed had little or no effect on the molecular mass of the synthesized PAN-based materials. The process variables interactions were statistically processed with the "F-test" method. Interaction between the initiator, AIBN and temperature had a significant effect on the average molecular mass. Monomer MA concentration was of little significance.

Keywords: viscosity, acrylonitrile, methylacrylate, initiator, concentration, stirrer speed, polymerization temperature

Received 30 May 2001; in final form 23 June 2001.

Permanent address of E. R. Sadiku is Tshwane University of Technology, Department of Polymer Technology, Postnet Suite 186, Private Bag X025, Lyhnwoodridge 0040, South Africa.

Address correspondence to R. D. Sanderson, UNESCO Associated Centre for Macromolecules and Materials Science, Dept. of Chemistry, University of Stellenbosch, Private Bag XI, Matieland 7602, Republic of South Africa. E-mail: rds@maties.sun.ac.za

INTRODUCTION

Although the copolymerization of acrylonitrile (AN) with methylmethacrylate (MA) has been extensively investigated [1, 2], little information is reported on the interactions between variable factors that influence the copolymerization process and the properties of the copolymer, especially molecular mass. The polymerization of acrylic acid was reported by Renard and McKenna [3], who concluded that the initiator and surfactant concentrations had little effect on the rate of reaction. However, for a minimum concentration of the monomer and maximum stirring rate, the activation energy was high. In another study, Benda et al. [4] investigated the inverse suspension polymerization of hydrophilic acrylic monomers in the static (non-stirred) continuous phase for the preparation of spherical polymeric beads of high molecular weight sodium polyacrylate. The two-stage, bulk polymerization of methyl methacrylate (MMA) in a continuously stirred tank was reported by Carrat et al. [5], who concluded that the stirred tank method improves temperature control and product uniformity in the early stages of the polymerization. It also eased the delivery of prepolymer to the second stage at the desired conversion and molecular weight.

The influencing factors, such as monomer concentration, amounts of initiator and chain transfer agent, on the molecular weight of the sodium salt of low molecular weight polyacrylic acid, were discussed by Lu and Zhu [6]. The operational conditions (conversion of monomer, concentration of polystyrene in oil phase and the impeller speed at the emulsification stage) that changed step-wise for the preparation of microcapsules containing water-absorbent sodium polyacrylate were discussed by Tanaka et al. [7]. These conditions were found to affect several properties of the microcapsules, such as the size distribution, the mean size, the content of core material, the rate of absorption of the prepared polymer and the amount of the absorbed water.

Lyoo et al. [8] polymerized AN in dimethylsulfoxide (DMSO) and also in tertiary butyl alcohol (TBA) at temperatures between 30 and 50°C using a moderate-temperature initiator 2, 2′-azobis (2, 4-dimethylvaleronitrile) (ADMVN). They then investigated the effects of the type and amount of solvent, polymerization temperature and initiator concentration on the polymer. They found that moderate polymerization temperature, using ADMVN, proved to be successful in obtaining PAN of high molecular weight and high conversion, with 2 small temperature rise during polymerization. For the same polymerization conditions, DMSO was found to be slightly superior to TBA in increasing the molecular weight of PAN and, on the other hand, DMSO was inferior to TBA in causing conversion to polymer. This indicates that the initiation rate of AN in DMSO was less than in TBA. The relationship between the viscosity and temperature of PAN/DMSO solution was reported by Xu and Wu [9] to follow an Arrhenius-type equation. The viscosity increased accordingly with the increase of molecular weight and concentration.

Zhang et al. [10] observed a decreasing power-law index, with increasing molecular weight of the copolymer and the solution concentration, but with decreasing solution temperature for a non-Newtonian PAN/DMF spinning solution, but with decreasing solution temperature. They also found that the viscosity flow activation energy increased with increasing spinning solution viscosity. Zhang et al. [11] prepared a high molecular weight PAN fiber by suspension polymerization of AN with AIBN as initiator and poly(vinyl alcohol) (PVA) as suspending agent. The effects of process conditions (polymerization temperature, suspension agent and initiator concentration) on the polymer were investigated and a kinetic model for the reaction was established.

According to Hu et al. [12], the entanglement structure in the solution viscosity system of ultra-high molecular weight polyacrylonitrile (UHMW-PAN) was destroyed after high speed stirring. They concluded that the solution concentration was improved by decreasing the viscosity to meet the requirement for the production of high performance gel-spun PAN fibers.

In this paper, we examine the influence of the process variables: monomer (MA) and initiator (AIBN) concentrations, stirrer speed and the polymerization temperature on the molecular mass of a copolymer of MA and AN. This was done to establish a favorable protocol that will enable the production of AN/MA copolymers of any desired molecular mass.

EXPERIMENTAL

Copolymers of methylacrylate (MA) and acrylonitrile (AN) were prepared under various conditions and dilute solution viscometry measurements were conducted using an Ubelode viscometer. The process variables that influence the molecular mass (and hence viscosity) were studied. The responses to the process variables were statistically analyzed (using the “F-test” method) for the different treatment combinations (MA and AIBN concentrations, polymerization temperature and AIBN concentration, MA concentration and stirrer speed, and polymerization temperature and MA concentration).

Synthesis of AN/MA Copolymers

The experimental set-up used for the polymerization reaction has been described elsewhere [13].

Preparation of AN/MA Copolymer Solution for Viscometry Measurements

36 g of the AN/MA copolymer and 4 g of polyvinylpyrrolidine (PVP) were added to 360 g of analytical grade DMSO [14, 15]. The mixture was vigorously shaken until a uniform suspension was formed. The mixture was subsequently stirred overnight or until all the solids had dissolved. Homogeneity of the solution was best obtained by gentle agitation for a few hours on rollers. Although the solution was relatively clear, any gel particles had to be removed prior to use for spinning. A warm solution (at 55°C) was filtered through a stainless steel filter (5 μm sieve size) at 3 bar nitrogen pressure. Air bubbles and dissolved gas in the filtered solution were removed by degassing the solution overnight, under vacuum.

Factorial Design for PAN Copolymers

The factorial design has been described elsewhere [13]. The process variables used in the factorial design at two levels and the complete experimental design with treatment combinations are shown in Table 1(a and b), while the amounts of monomers, solvents and the polymerization conditions are summarized in Table 2.

Viscometry Measurements

Using an Ubbelohde viscometer, dilute solution viscosity measurements were carried on eight AN/MA copolymers synthesized, to determine

TABLE 1A Process Variables Used in the Factorial Design at Two Levels

Factor	Variable	Unit	Description	Level (*llf*)	Level (*hlf*)
A	Initiator	g	Amount of initiator	0.2625	0.4125
B	MA	g	Amount of MA	0.6830	2.73
C	Temperature	°C	Polymerization temp.	60.00	70.00
D	Stirrer speed	rpm	Speed at which suspension is stirred	50.00	159.00

llf = low level factor, *hlf* = high level factor.

TABLE 1B The Complete Experimental Design, with Treatment Combinations Having a Half Replicate For a 2^4 Factorial

Standard run order	Factor A	Factor B	Factor C	Factor D	Treatment combination
1	*llf*	*llf*	*llf*	*llf*	–
2	*llf*	*llf*	*hlf*	*hlf*	CD
3	*llf*	*hlf*	*llh*	*hlf*	BD
4	*llf*	*hlf*	*hlf*	*llf*	BC
5	*hlf*	*llf*	*llf*	*hlf*	AD
6	*hlf*	*llf*	*hlf*	*llf*	AC
7	*hlf*	*hlf*	*llf*	*llf*	AB
8	*hlf*	*hlf*	*hlf*	*hlf*	ABCD

llf = low level factor, *hlf* = high level factor.

the average molecular mass of each of the copolymers. Dimethylformamide (DMF) was used as solvent for the synthesized copolymers and the analyses were done at 30°C. A concentration range of AN/MA copolymer in DMF was prepared for each analysis. An average time value within ± 1% error range was accepted. The viscosity average molecular mass, $\bar{M}_v$c, was obtained using the Mark-Houwink-Sakurada relation [16]: $[\eta] = kM_v^{\alpha}$, where $[\eta]$ is the intrinsic viscosity of the dilute polymer solution, k ($= 0.0209$) and α ($= 0.75$) are constants.

TABLE 2 Actual Amounts of Monomers and Solvents, and the Polymerization Conditions

Run, (Random order)	Run, (Standard order)	DMF, g	AN, g	MA, g	AIBN, g	Temp., °C	Stirrer speed, rpm
2	1	54.04	36.02	0.27	0.21	60	1.0
7	2	54.02	36.02	0.27	0.21	70	3.5
3	3	54.01	36.04	1.02	0.21	60	3.5
8	4	54.00	36.00	0.34	0.21	70	1.0
1	5	54.12	36.00	0.24	0.33	60	3.5
5	6	54.02	36.00	0.25	0.331	70	1.0
6	7	54.00	36.01	0.99	0.336	60	1.0
4	8	54.00	36.00	0.98	0.33	70	3.5

DMF = Dimethylformamide, AN = Acrylonitrile, MA = Methylacrylate,
AIBN = Azo-bis-isobutyronitrile.

RESULTS AND DISCUSSION

Analysis of Variance

The total of each of the main factors and the two factor interactions were obtained by subtracting the sums of the responses at the high levels from the sums of the responses at the low levels. The effect of each factor was then calculated by dividing each total by four (the number of values for each sum). The sum of squares was calculated thus:

$$\text{Sum of Squares, SS} = (\text{Total of main factors})^2 \div 8 \qquad (1)$$

The numerator in the equation correlates to the total number of experiments carried out. A single-sided "F-test" was performed on each of the treatment combinations to determine the probability of percentage level of significance. Each of the treatment combinations has only one degree of freedom and, therefore, the mean sum of squares is equal to the sum of squares. Table 3 gives a detailed procedure followed in performing the "F-test", while Tables 4 and 5 show the response (intrinsic viscosity and hence molecular mass) and the F-ratios respectively, resulting from the different treatment combinations. The calculated estimate of error variance (used to determine the F-ratios for each of the treatment combinations) is shown in Table 6. From the results of the "F-test", it was clear that none of the factors had a significant influence on any of the responses. The chance of being wrong when postulating that any one of the factors had a significant influence is greater than 10% in the case of each treatment combination for each of the responses. In statistical terms, this is very large. It must be remembered, however, that this is true only for the range in which each factor was varied. It can be concluded, therefore,

TABLE 3 Procedure for Performing the 'F-Test'

Treatment combination	Total	Effect	Degrees of freedom	Sum of Squares
A	104059.20	26014.8	1	13.50×10^8
B	52861.77	13215.4	1	3.49×10^8
C	− 107025.12	− 26756.3	1	14.30×10^8
D	63251.73	15812.9	1	5.00×10^8
$AB \equiv CD$	118493.57	29623.4	1	17.60×10^8
$AC \equiv BD$	111829.71	27957.4	1	15.60×10^8
$AD \equiv BC$	65637.30	16409.3	1	5.40×10^8
Total			7	75.00×10^8

TABLE 4 Viscometry Data for AN/MA Copolymers

Batch #	Intrinsic viscosity	Average mol. mass (g.mol^{-1})
1	120.24	103082
2	161.89	153255
3	152.39	141387
4	187.70	186679
5	165.94	158392
6	153.40	142639
7	127.63	111618
8	106.12	87270

TABLE 5 Response (Average Molecular Mass) from the Treatment Combination

Treatment combination	Degrees of freedom	Sum of squares ($\times 10^8$)	F-ratio	% level of significance
A	1	13.50	1.05	>10
B	1	3.49	0.27	>10
C	1	14.30	1.11	>10
D	1	5.00	0.39	>10
AB ≡ CD	1	17.60	1.37	>10
AC ≡ BD	1	15.60	1.21	>10
AD ≡ BC	1	5.40	0.42	>10
Total	7	74.89		

TABLE 6 Estimate of Error Variance for the Responses

Response	Estimate of error variance
Average mol. mass	1.29×10^9

Due to confounding, a true error variance can not be calculated. However, an estimate of the error of the variance can be assumed. This was done using the sum of squares of the two-factor interaction. This can be done because the two factor interactions are confounded with each other. The equation below shows how the estimate of error variance was calculated. The values of the SS used, are those in Table 6 above.

$$\text{Estimate of error of variance} = \frac{\text{SS}(\text{AB} \equiv \text{CD} + \text{AD} \equiv \text{BD} + \text{AD} \equiv \text{BC})}{3}$$

that although a factor does not have a significant effect, it can still have an influence on the various responses. The influence of the different process variables on the various responses was determined by comparing the sum of squares value of each treatment combination with that of the estimate of error variance. If the sum of squares value of a treatment combination is higher than that of the estimate of error variance, then the factor is said to have an influence on the response. The discussion on the influence of each of the factors on the process responses was based on this assumption. Table 7a shows the factors (and the interactions of factors) that have influence in the case of each response.

Figure 1 shows that a high AIBN concentration with a high MA concentration yielded a polymer of high average molecular mass. The MA seemed to have a large effect on the response, in contrast with the analysis of variance. The interaction of MA and AIBN, however, seems to have a considerable influence, as shown in Figure 1. The effect of the two-factor interaction observed is with AIBN and MA, and not that of temperature and stirrer speed. Again, AIBN did not seem to have an influence at low polymerization temperatures, as reflected in Figure 2. High molecular mass AN/MA was obtained at both high and low AIBN concentrations at low polymerization temperature, and similarly with high AIBN concentration and high polymerization temperature. From the analysis of variance it can be seen that both AIBN and the polymerization temperature have a large influence on the response. From Figure 2, the interaction of AIBN concentration with temperature had a significant effect on the average molecular mass. Therefore, the two-factor interaction of temperature and AIBN (and not that of MA and stirrer speed) permitted a high molecular mass of the copolymer produced.

A high molecular mass of AN/MA copolymer was obtained at high MA concentration and high stirrer speed interaction as shown in Figure 3. The influence of the stirrer speed on the observed response did not seem to be significant. Both high and low MA concentrations at low polymerization temperature, on the one hand, as well as high MA concentration with high polymerization temperature, on the other

TABLE 7A Factors (and Their Combinations) that Have Influence on the Responses

Response	A	B	C	D	AB ≡ CD	AC ≡ BD	AD ≡ BC
Average mol. mass	✓		✓		✓	✓	

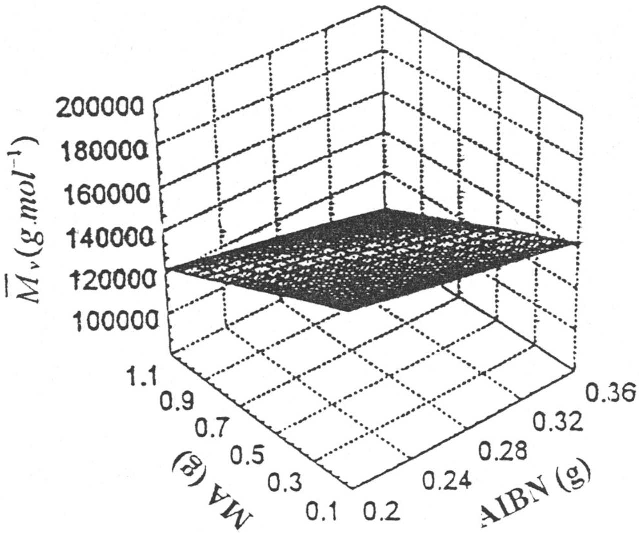

FIGURE 1 Average molecular mass (λ) of AN/MA copolymer as a function of AIBN (β) and MA (γ) concentrations.

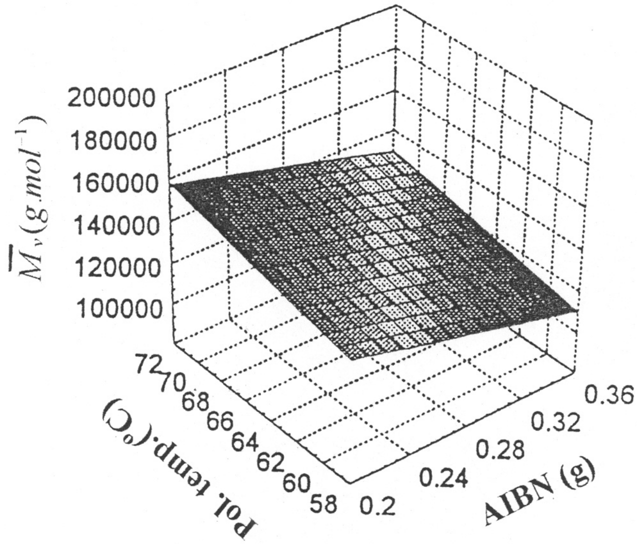

FIGURE 2 Average molecular mass (λ) of AN/MA copolymer as a function of polymerization temperature (γ) and AIBN (β) concentration.

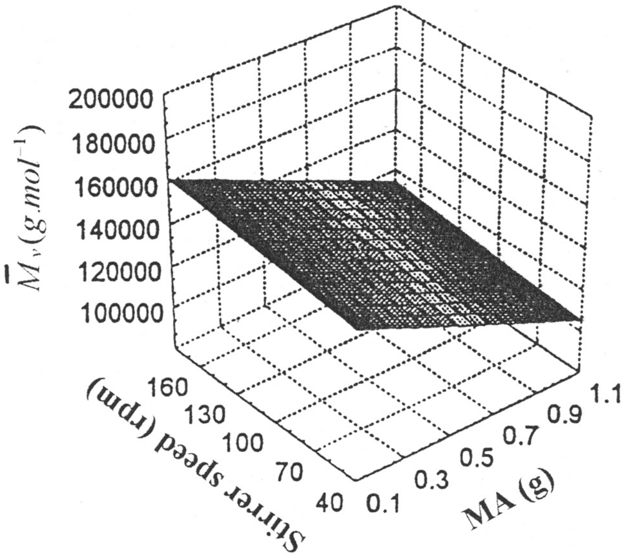

FIGURE 3 Average molecular mass (λ) of AN/MA copolymer as a function of MA concentration (β) and the stirrer speed (γ).

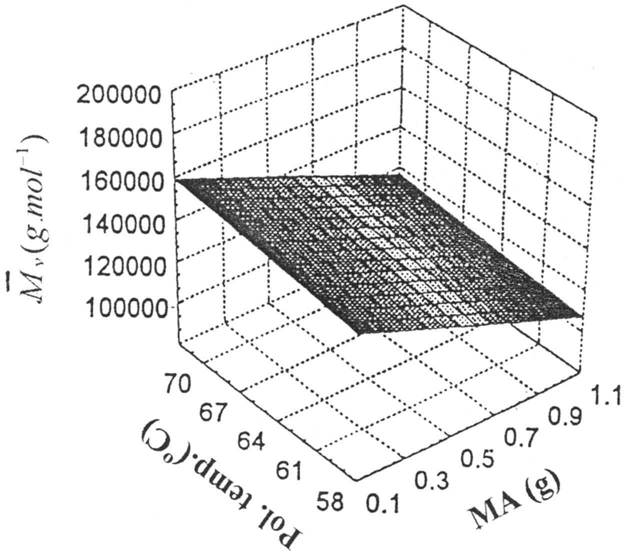

FIGURE 4 Average molecular mass (λ) of AN/MA copolymer as a function of polymerization temperature (γ) and MA concentration (β).

TABLE 7B Factors That Have Influence on the Responses

Process variables	Level
AIBN	*hlf* (+)
Stirrer speed	*hlf*/*llf* (+/−)
MA	*hlf* (+)
Polym. temp.	*llf* (−)

hlf: high factor (+ contribution to high molecular mass).
llf: low level factor (− contribution to high molecular mass).
hlf/*llf*: variable with indifference response(s).

hand, yielded a high molecular mass. However, low MA concentration at high polymerization temperatures yielded low molecular mass AN/MA copolymer. An estimate response function plot of MA concentration, stirrer speed and average molecular mass, Figure 3, shows that a high MA concentration with high stirrer speeds yielded high average molecular mass AN/MA. From Figure 4 it can be seen that low polymerization temperature with high MA concentration yielded high average molecular mass AN/MA copolymer. The highest molecular mass AN/MA copolymer is obtainable with the process variables, as detailed in Table 7b.

CONCLUSIONS

Process variables such as stirrer speed, polymerization temperature, MA and AIBN concentrations have influences on the properties of the AN/MA copolymer produced and hence on the properties of the membranes produced. In particular, high and low MA concentrations and low polymerization temperature, on the one hand, and high MA concentration with high polymerization temperatures, on the other hand, produced a high molecular mass copolymer. The interaction of high AIBN concentration and high stirrer speed produced a high molecular mass copolymer. The stirrer speed showed some indifference in the response of the molecular mass of the copolymer obtained, while the MA and AIBN concentrations produced high molecular masses of AN/MA copolymers and the polymerization temperature did not affect the response significantly.

REFERENCES

[1] Koresh, J.E., Soffer, A. (1983). *Sep. Sci. Technol.*, **18**(8), 723.
[2] Koresh, J.E., Soffer, A. (1987). *Sep. Sci. Technol.*, **22**(2), 973.
[3] Renard, B., McKenna, T.F. (2000). *Macromol. Symp.*, **150**, 251.

[4] Benda, D., Snuparek, J., Cermak, V. (1997). *J. Dispersion Sci., Tech.*, **18**(2), 115.

[5] Carratt, G.M., Shervin, C.R., Soong, D.S. (1984). *Polym. Eng. Sci.*, **24**(6), 442.

[6] Lu, J., Zhu, X. (1994). *Huaxue Shijie (Chinese)*, **35**(9), 471.

[7] Tanaka, M., Sato, K., Kimura, I. (1991). *Shikizai Kyokaishi (Japanese)*, **64**(3), 140.

[8] Lyoo, W.S., Ghim, H.D., Yoon, W.S., Lee, J., Lee, H.S., Ji, B.C. (1999). *Eur. Polym. J.*, **35**(4), 647.

[9] Xu, L., Wu, H. (1999). *Beijing Huagong Daxue (Chinese)*, **26**(3), 21.

[10] Zhang, G.-P., Mao, P.-J., Zhang, I., Yang, M.-Y., Wang, R.-G. (1999). *Gongcheng Jishuban (Chinese)*, **14**(3), 26.

[11] Zhang, I., Yang, M., Mao, P. (1998). *Hecheng Xianwei Gongye (Chinese)*, **21**(4), 29.

[12] Hu, P., Zhu, D., Zhao, J., Wu, C., Qian, B. (1998). *Hecheng Xianwei Gongye (Chinese)*, **21**(3), 10.

[13] Sanderson, R.D., Sadiku, E.R. (2001). *Int. J. for Polymeric Materials*, **52**(11).

[14] Linkov, V.M., Sanderson, R.D., Jacobs, E.P. (1994). *Polymer International*, **35**, 239.

[15] Gupta, A.K., Paliwal, D.K., Bajaj, P. (1991). *J. Macromol. Sci.-Rev.*, **C31**(1), 1.

[16] Collins, E.A., Bareš, J., Billmeyer (Jr.), F.W. (1973). *Experiments in Polymer Science*, New York: John Wiley and Sons.