Polymer Bulletin 47, 421-427 (2002)

Polymer Bulletin

The copolymerization of N-vinyl-2-pyrrolidone with 2-hydroxyethyl methacrylate

Magdy M. Faragalla[1], **David J. T. Hill**[1] (✉), **Andrew K. Whittaker**[2]

[1] Polymer Materials and Radiation Group, Department of Chemistry, University of Queensland,
QLD 4072, Australia
[2] Centre for Magnetic Resonance, University of Queensland, QLD 4072, Australia
e-mail: hill@chemistry.uq.edu.au, Fax: +61 7 3365 4299

Received: 27 Febuary 2001/Revised version: 5 November 2001/Accepted: 6 November 2001

Summary

The bulk free radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) with N-vinyl-2-pyrrolidone (VP) was carried out to low conversions at 50 °C, using benzoyl peroxide (BPO) as initiator. The compositions of the copolymers were determined using ^{13}C NMR spectroscopy. The conversion of monomers to polymers was studied using FT-NIR spectroscopy in order to predict the extent of conversion of monomer to polymer. From model fits to the composition data, a statistical F-test revealed that the penultimate model describes the copolymerization better than the terminal model. Reactivity ratios were calculated by using a non-linear least squares analysis (NLLS) and $r_H = 8.18$ and $r_V = 0.097$ were found to be the best fit values of the reactivity ratios for the terminal model and $r_{HH} = 12.0$, $r_{VH} = 2.20$, $r_{VV} = 0.12$ and $r_{HV} = 0.03$ for the penultimate model. Predictions were made for changes in compositions as a function of conversion based upon the terminal and penultimate models.

Introduction

Hydrogels are widely used as biomaterials and can be easily fabricated into a wide range of morphologies to meet the specified requirements of particular applications. Hydrogels based on HEMA have been used in many medical applications, such as in contact lenses, haemodialysis membranes, artificial skin, drug release systems [1,2,3], while those based on VP have also received wide use as biomedical materials [4,5,6].

As a result of this wide variety of applications, the copolymerization of HEMA and VP in solution has been studied, and the terminal model reactivity ratios for VP have been reported to be low while those for HEMA have been found to be large. For example, Al-Issa *et al.* [7] found that this system exhibited pronounced compositional heterogeneity, and reported reactivity ratios of VP and HEMA were 0.05 and 3.12 respectively for polymerization in ethanol. Reddy *et al.* [8] also studied this system to determine the reactivity ratios and the molecular weights of the polymers formed in solution in methanol and reported that the reactivity ratios were $r_V = 0.06 \pm 0.10$ and $r_{HEMA} = 4.35 \pm 0.04$ using the Fineman-Ross method and were $r_V = 0.02 \pm 0.14$ and $r_{HEMA} = 4.50 \pm 0.24$ using the Kelen-Tudos method. Most recently Gallardo *et al.* [9] used ^{1}H NMR to determine compositions in copolymers of VP and HEMA polymerized in water/ethanol solutions, and determined $r_V = 0.077$ and $r_{HEMA} = 7.97$.

In this paper, the bulk copolymerization of the HEMA/VP system has been studied, and the relation between the feed monomer composition and the copolymer composition examined. The reactivity ratios for both the terminal and penultimate models were evaluated, and the triad fractions and the change of feed composition with monomer conversion have been predicted.

Experimental

Materials and copolymer synthesis

N-vinyl-2-pyrrolidone (VP) and 2-hydroxyethyl methacrylate (HEMA) (Aldrich Chem. Co.) were purified by distillation under reduced pressure (4 mm Hg). The required amounts of VP, HEMA, and the initiator were accurately weighed to give the desired compositions and transferred into reaction ampoules, giving a concentration of the initiator of 0.05 M.

The mixtures were then subjected to three cycles of freeze-thaw-degassing to remove oxygen from the reaction mixture. The ampoules were then sealed under vacuum. The polymerization was facilitated by placing the sealed ampoules in a water bath at 50 ± 2 °C with agitation. The conversion was limited to less than 5% based on a study of the kinetics of the polymerization.

After polymerization, the mixtures were poured into an excess of diethylether to precipitate the copolymers. The precipitated copolymers were then filtered and dried under vacuum at room temperature. They were further purified by dissolution in ethanol and then re-precipitation in diethylether to remove any traces of the monomers. The polymers were then dried and weighed to estimate the conversion.

Instruments

FT-NIR spectra were obtained using a Perkin-Elmer 1600 FT-IR spectrometer. A computer program was used to collect spectra at 1-minute intervals. Spectra were obtained in the region 8000 – 4000 cm^{-1} with a resolution 8 cm^{-1} with 16 scans being accumulated. NMR spectra of the copolymers were recorded on a Bruker AMX 400 NMR spectrometer, using 15% (w/v) solutions in deuterated dimethyl sulphoxide (d6–DMSO) at 302 K.

Quantitative ^{13}C spectra of the copolymers were acquired with inverse gated decoupling with more than 3000 scans per spectrum, each containing 32 K data points. The pulse program used a 90° pulse angle of 7.2 µs with a 15 s relaxation delay.

Results and discussion

Mechanism of copolymerization

For a study of the copolymerizations of HEMA and VP, the relationship between the mole fractions of the component monomers in the feed and the copolymer has to be determined. Therefore copolymerizations of monomer mixtures having various feed compositions were carried out to low conversions in the presence of BPO as initiator at 50° ± 2°C.

In order to be able to predict the conversion of monomer to polymer, the rate of polymerization for HEMA and VP were monitored by FT-NIR spectroscopy. Bulk solutions containing the monomer and the initiator were transferred to glass tubes with an i.d. ≈ 3 mm, degassed using the usual freeze-thaw-degas cycles and sealed under vacuum. The tubes were then placed in a heating block that was equilibrated at 50° ± 2°C mounted in the spectrometer. Figure 1 shows the NIR spectra of HEMA and VP without added initiator. An estimation of the time required to reach ≈ 5% conversion was obtained by monitoring the rate of the decrease of the area of the >C=CH– overtone band at 6170 cm^{-1}. The fractional conversion was calculated from the decrease in intensity of this peak compared with the initial intensity. Figure 2 shows the experimental data for the time dependence of the monomer concentrations for HEMA and VP. The curves indicate that the rate of polymerization of HEMA is faster than that of VP.

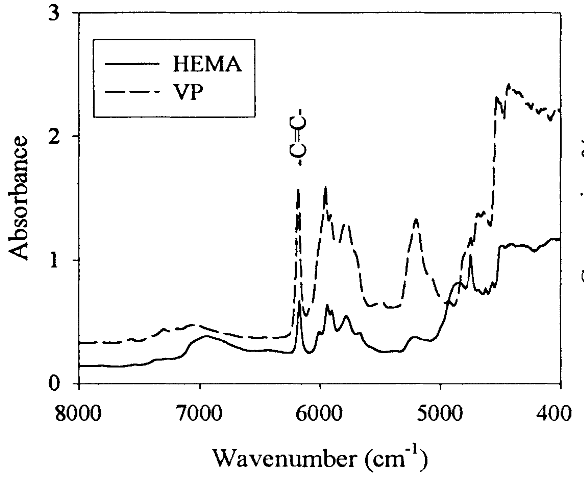


Figure 1. FT-NIR spectra of HEMA and VP monomers

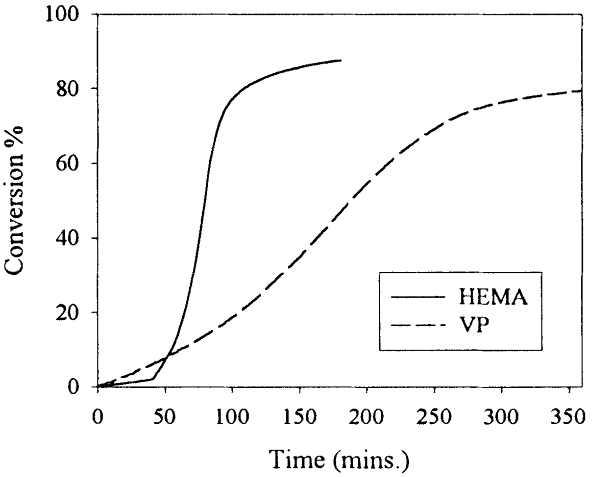


Figure 2. Conversion of HEMA and VP to polymer during homopolymerization at 50 °C

Copolymers polymerized to conversions of less than 5% at various monomer feed compositions were characterized as described above and Figure 3 shows the ^{13}C spectrum of the copolymer prepared from a mixture of mole fraction of VP, f_{VP} = 0.8457, and is representative of the ^{13}C spectra of all the copolymers. Assignments to the spectra shown on the figure were made by comparison with literature spectra.

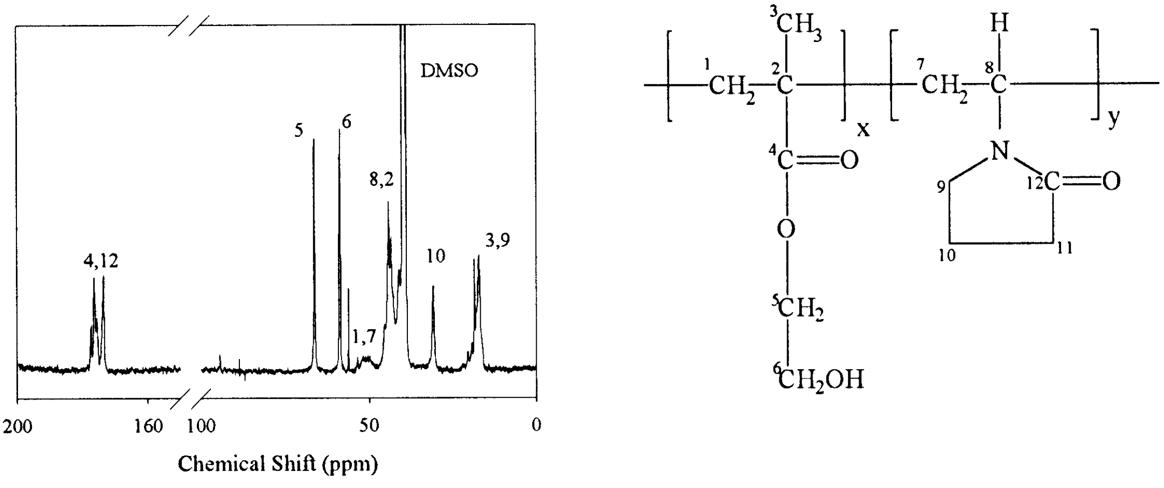


Figure 3. Quantitative ^{13}C NMR spectrum of poly(HEMA-co-VP) with f_{VP} = 0.8457

The proportions of the two monomers in the copolymers can be found by analysis of the peak areas labelled C_{10} and C_5, as these are well-resolved peaks. The calculated copolymer compositions are tabulated in Table 1 and are shown in Figure 4.

Table 1. Comonomer (f_{VP}), conversion and copolymer (F_{VP}) compositions expressed as mole fractions of VP from experiment (Exp), and model predictions, terminal (TUM) and penultimate (PUM), for bulk copolymerization of VP and HEMA at 50°C.

ID	f_{VP}	F_{VP} (Exp)	F_{VP} (TUM)	F_{VP} (PUM)	% Conversion
V95H05	0.9503	0.67	0.683	0.670	2.7
V90H10	0.9008	0.51	0.511	0.511	2.7
V85H15	0.8457	0.41	0.361	0.402	2.7
V80H20	0.7999	0.33	0.326	0.337	4.3
V70H30	0.7002	0.23	0.220	0.221	3.1
V60H40	0.6011	0.14	0.154	0.145	2.2
V50H50	0.5019	0.094	0.109	0.097	2.2
V40H60	0.4033	0.073	0.076	0.063	2.2
V30H70	0.3034	0.042	0.051	0.040	3.1
V2080	0.2076	0.017	0.031	0.023	3.2

With the knowledge of the comonomer and copolymer compositions, the reactivity ratios were determined by fitting the composition data to the copolymer equations for the terminal and penultimate models [10,11]. A minimization procedure based on the NLLS analysis was employed which also accounted for the level of conversion of the monomers [11]. From statistical analyses, using the F-test [11], it was determined that there is an improvement in the fit of the penultimate model over the terminal model at a level of confidence of 95%. Since the reactivity ratios are determined simultaneously and hence are not stastically independent, there exists a volume of space (joint confidence region) within which the true set of parameters is believed to lie with a given level of certainty. The 95% and 99% confidence levels for the terminal model and the penultimate model are presented in Figures 5 and 6, respectively. The best values of the reactivity ratios based on the terminal model are $r_H = 8.18$ and $r_V = 0.097$ for HEMA and VP, respectively, while those based on the penultimate model are $r_{VV} = 0.12$, $r_{VH} = 0.03$, $r_{VH} = 2.20$, $r_{HH} = 12.0$. The predicted copolymer compositions obtained for the two models for the experimental feed compositions are given in Table 1.

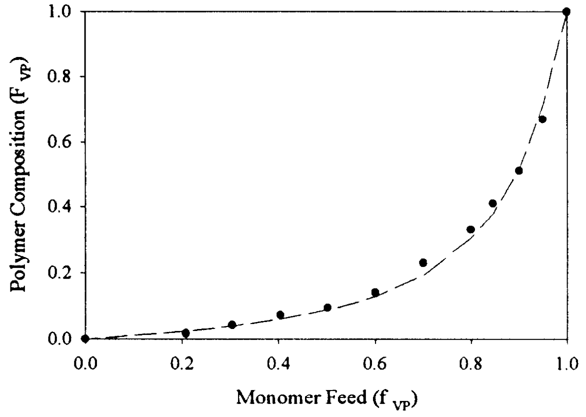


Figure 4. Copolymer composition versus comonomer feed

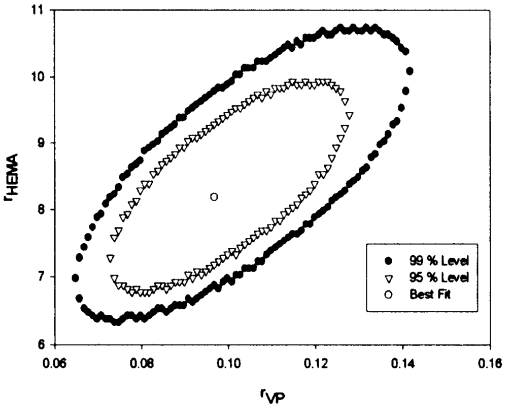


Figure 5. The joint confidence levels for the terminal model

Table 2. Statistical parameters for the fit of the composition data to the terminal and penultimate models.

	Terminal model	Penultimate model
SS (Θ)	0.005	0.0004
S_Y	0.025	0.008

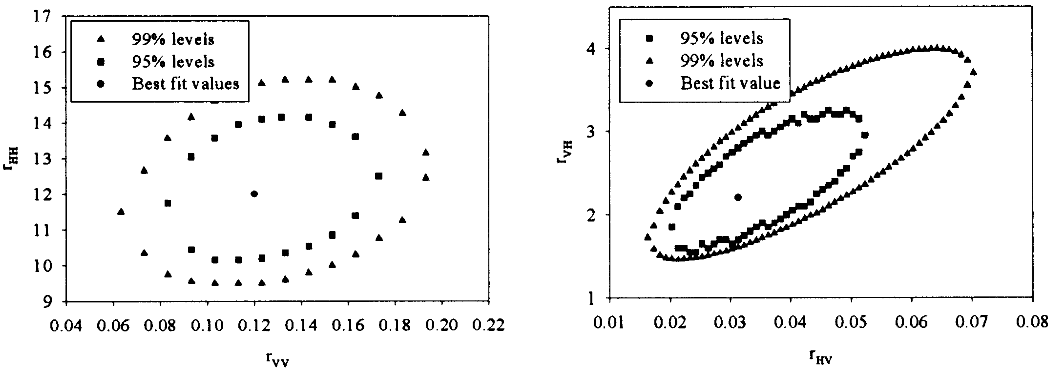


Figure 6. The joint confidence levels for the penultimate model.

The statistical parameters for both the terminal and penultimate models are tabulated in Table 2. For the terminal model, the value of $r_H > 1$ indicates that the rate constant of propagation k_{HH} is greater than k_{HV}, which reflects the great tendency for homopropagation of HEMA at the HEMA chain end radical. The value of $r_V < 1$ indicates that the rate constant of propagation k_{VH} is greater than k_{VV} which demonstrates the great tendency for crosspropagation and addition of HEMA at the VP chain end radical. The values of the two terminal model reactivity ratios are of similar magnitude to the corresponding values reported by Gallardo *et al.* [9] for polymerization in water/ethanol mixtures at 50°C, but they differ from the values reported by Al-Issa *et al.* for polymerizations in ethanol at 65°C and those reported by Reddy *et al.* [8] for polymerizations in methanol at 50°C. Indeed, the products of the two reactivity ratios for the three solvent systems are respectively 0.61, 0.16 and 0.09, while that found herein for bulk polymerization was 0.79. This variation in the product of the reactivity ratios from system to system suggests that the simple solvent partitioning model suggested by Harwood [12], which requires that the product of the reactivity ratios is constant from system to system, cannot account for the observed results. Indeed the reactivity ratio for HEMA increases in value as the solvent polarity increases.

For the penultimate model, the values of $k_{HHH} / k_{HHV} = 12.0$ and $k_{VHH} / k_{VHV} = 2.20$ indicate a more significant effect of the HEMA penultimate unit and the great tendency for homopropagation of HEMA. For VP, the values of $k_{VVV} / k_{VVH} = 0.12$ and $k_{HVV} / k_{HVH} = 0.03$ indicate a more significant penultimate effect for the HEMA unit leading to the cross propagation. The origin of the HEMA penultimate unit effect is presumably the hydroxy group in the HEMA units, which would be capable of hydrogen bonding to adjacent groups and so influencing the rate of addition of HEMA units to the chain end radicals. The magnitude of the observed penultimate unit effect is relatively large, being 6 times for the HEMA chain end radicals and 4 times for the VP chain end radical. This compares with values of approximately 3 times for the penultimate unit effects in polymerizations of styrene and acrylonitrile [11]. However, the larger effect observed for HEMA may not be surprising given the highly polar nature of the hydroxyl group.

The sequence distribution

The instantaneous sequence distributions can be calculated across the range of comonomer compositions for the terminal and penultimate models using the appropriate reactivity ratios [11]. The HEMA- and VP-centred triad distributions for each copolymer have been plotted against the feed composition and are displayed in Figure 7. Unfortunately, experimental estimates of the sequence triad fractions cannot be determined from the NMR spectra, so they are unavailable for use as a test for the predictions of the models. The predictions for the two models differ somewhat, but the overall trends are similar. The figures show that HHH sequences predominate up to high content of VP (80%) confirming the predominant tendancy towards homopropagation of HEMA units. On the other hand, the VP-centred sequences have a HEMA unit as one neighbour for all copolymers with VP content lower than 80%, demonstrating the tendency for crosspropagation of VP chain-end radicals.

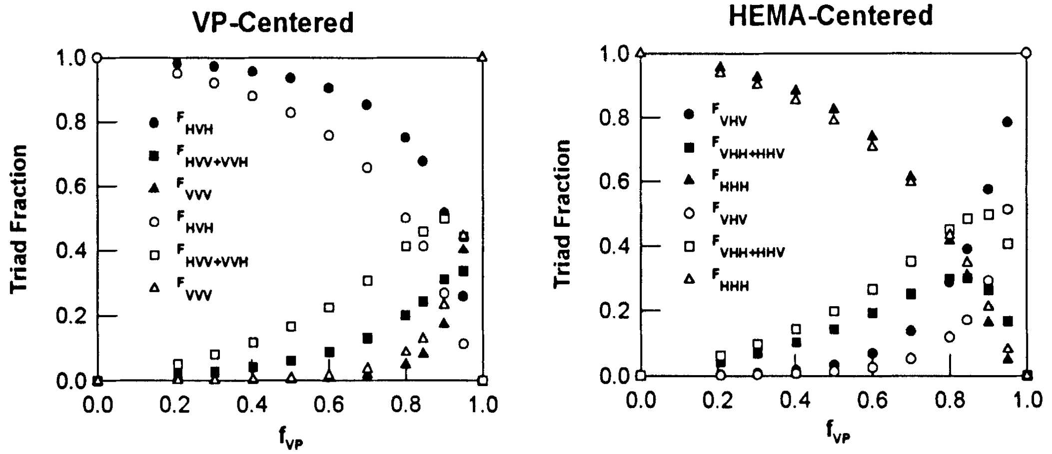


Figure 7. The triad fraction distributions for VP and HEMA centred triad versus VP composition of initial monomer feed. The open symbols are for the terminal model and the closed symbols are for the penultimate model.

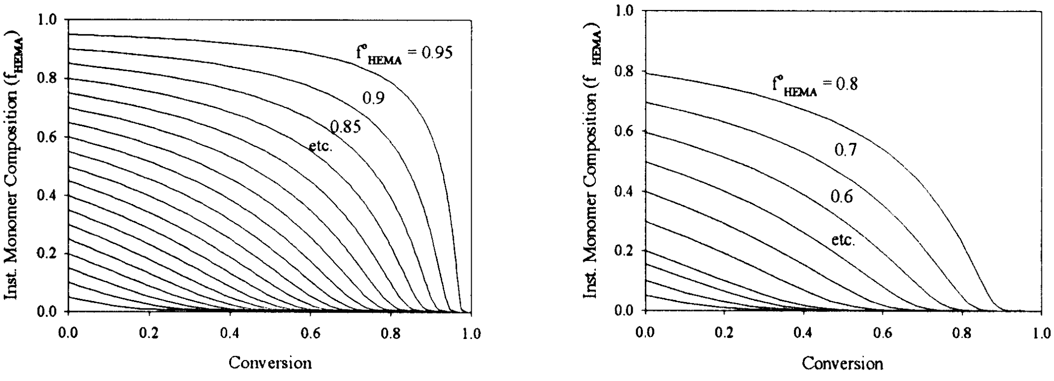
The copolymer composition at high conversion

The change in a monomer mixture composition during copolymerization was first studied by Skeist [13] who provide convenient equations for the calculation of the composition distribution curve for the terminal model. Meyer and Lowry [14] developed an analytical solution to Skeit's equation. For $r_1 \neq 1$ and $r_2 \neq 1$ they obtained:

$$M/M_0 = (f_1 / f_1^0)^{\alpha} (f_2 / f_2^0)^{\beta} \; [(f_1^0 - \delta) / (f_1 - \delta)]^{\gamma}$$

where M and M_0 represent the total number of moles present in the monomer feed at a given time t and at time 0, respectively, $\alpha = [r_2/ (1 - r_2)$, $\beta = [r_1 / (1- r_1)]$, $\gamma = [(1 - r_1r_2) / (1 - r_1)(1 - r_2)]$, $\delta = [(1 - r_2) / (2 - r_1 - r_2)]$. Using this equation and the reactivity ratios calculated for the terminal model, the feed monomer change was calculated and plotted as a function of conversion in Figure 8, where the conversion = 1-(M/M_0). This method has been described in detail recently by Gallardo *et al.* [9].

The corresponding data for the penultimate model have been calculated using the programs we have described previously [11]. These data are also shown in Figure 8.



A **B**

Figure 8. The change in instantaneous composition of the monomer feed with conversion; (A) Terminal model, (B) Penultimate model.

The data in Figure 8 show that there is no azeotropic composition in this system and indicate that both models predict that HEMA will be depleted in the monomer feed as the polymerization proceeds to high conversion. These observations have important consequences for HEMA/VP copolymerizations carried out in bulk to high conversions, as is done for some biological applications of these materials.

Conclusions

The bulk copolymerization of HEMA and VP at 50 °C was found to be best described by the penultimate model. The reactivity ratios were found to be r_H = 8.18 and r_V = 0.097 for the terminal model and r_{HH} = 12.0, r_{HV} = 2.20, r_{VV} = 0.12 and r_{VH} = 0.03 for the penultimate model. These reactivity ratios were used to predict the instantaneous copolymer compositions and sequence distributions as a function of the monomer feed. The change of the monomer feed composition with the conversion was calculated using the reactivity ratios for both of the models. It was found that in this system there is no azeotropic composition and HEMA is depleted as the polymerization proceeds to high conversion.

Acknowledgements.

The authors would like to acknowledge financial assistance from the Australian Research Council and the University of Queensland.

References

1. Young CD, Wu JR, Tsou TL (1998) Biomaterials 19: 1745
2. Trigo RM, Blanco MD, Huerta P, Olimo R, Teijon JM (1993) Polymer Bull. 31: 577
3. Gokce M, Akata RF, KiremitciGumusderelioglu M (1996) Biomaterials 17: 941
4. Hying C, Staude E (1998) J. Memb. Sci. 144: 251
5. Hwang JR, Sefton MV (1995) J. Memb. Sci. 108: 257
6. Kim CS, Lee CH, Shin JS, Hyung NI (1997) Nuclic Acid Research 25:1085
7. Al-Issa MA, Davis TP, Huglin MB, Yip DCF(1985) Polymer 26:1869
8. Reddy BSR, Arshady R, George MH (1985) Eur. Polym. J. 21: 511
9. Gallardo A, Lemus AR, Roman JS, Cifuentes A, Diez-Masa JC (1999) Macromolecules 32: 610
10. O’Driscoll KF, Reilly PM (1987) Makromol. Chem., Macromol. Symp. 10/11:355
11. Hill DJT, O’Donnell JH (1987) Makromol. Chem., Macromol. Symp. 10/11:375
12. Harwood HJ (1987) Makromol. Chem., Macromol. Symp. 10/11:331
13. Skeist I (1946) J. Am. Chem. Soc. 68: 1781
14. Meyer VE, Lowry GC (1965) J. Polym. Sci. A3:2843