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Molecular Weight Characteristics of 2-Naphthyl Methacrylate Copolymers Obtained by Radical Polymerization in Different Solvents

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Dedicated to Professor Ivan M. Panayotov to his 60. birthday with the best wishes

SUMMARY

The influence of the chemical nature of the polymerization medium on the molecular weight characteristics of the copolymers 2-naphthyl methacrylate/styrene and 2-naphthyl methacrylate/acrylonitrile was investigated by gel permeation chromatography. The results obtained show that the influence of the nature of the solvent used on the molecular weight characteristics could be attributed to the different chain transfer constants. The contribution of the monomer complexes which affects mainly the relative reactivity ratios of the comonomers may be neglected.

INTRODUCTION

As it is known different factors may influence the radical polymerization: dipole-dipole and donor-acceptor interactions, H-bonding, the chemical nature of the solvent etc (1). It has been established that the polarity of the solvent is of primary importance and influences the rate of polymerization as well as the tacticity of the polymers obtained. By means of IR- and ^{1}H-NMR spectroscopy mainly the influence of the reaction medium on the relative reactivity ratios has been studied. It is interesting to know how the chemical nature of the solvent affects the molecular weight and the molecular weight distribution which determine the mechanical, rheological and other properties of the copolymers obtained. The knowledge of these molecular weight characteristics (MWC) may enlighten the mechanism of polymerization.

A fast and convenient method for obtaining these characteristics is the gel permeation chromatography (GPC). Using this method poly(2-naphthyl methacrylates) obtained in different solvents as well as copolymers 2-naphthyl methacrylate/methyl methacrylate and benzyl methacrylate/methyl methacrylate have been sdudied (2).

There are no data for the MWC of other 2-naphthyl methacrylate copolymers. The present paper represents an attempt to investigate via GPC the influence of the chemical nature of the interaction medium - chloroform, benzene, 1,4-dioxane, acetone and acetonitrile, on the molecular weight characteristics (molecular weight and molecular weight distribution) of copolymers 2-naphthyl methacrylate/styrene (2-NM/St) and 2-naphthyl methacrylate/acrylonitrile (2-NM/AN).

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EXPERIMENTAL

Materials

The initiator 2,2'-azoisobutyronitrile (AIBN) was recrystallized from alcohol, m.p. 102-103°C.

2-Naphthyl methacrylate (2-NM) was synthesized according to (3). Acrylonitrile (AN) and styrene (St) were used after distillation.

Chloroform, benzene, 1,4-dioxane and acetonitrile were dried and distilled prior to use.

Copolymerization

In glass ampoules to a 1 mol/L monomer solution 0,5 mol % (for 2-NM/St) and 1,0 mol % (for 2-NM/AN) AIBN were added. After degazation the sealed ampoules were heated in a thermostat at 60°C for a definite time. In all cases investigated, the copolymers formed in acetonitrile precipitated during polymerization. In the other solvents the polymerization was homogeneous. In all experiments the conversion was about 10 %. The copolymers obtained were precipitated and dried under reduced pressure by known methods (4,5).

Measurements

The GPC analyses were performed on Waters equipment consisting of an automatic injector WISP 710 B, M 510 pump, R 401 differential refractive index detector (DRI) and M 440 UV detector ($\lambda = 254$ nm). A set of four Ultrastyragel columns with pore sizes 10^5, 10^4, 10^3 and 500 Å was used. The flow rate of the mobile phase - tetrahydrofuran, was 1 mL/min at 35°C.

The molecular weights of the copolymers investigated were calculated towards polystyrene standards using Waters M 730 Data Module. By the modified method of the universal calibration (6) it was found out that the relations of the elution volumes and the molecular weights for the homopolymers of 2-NM, St and AN lie on the same straight line. For the purpose we used low molecular weight poly-AN, as the high polymers of AN were poorly soluble in tetrahydrofuran.

For all copolymers full correspondence of the elution curves obtained by both (DRI and UV) detectors was found.

RESULTS AND DISCUSSION

At the polymerization of 2-NM (7) and its copolymerization with methyl methacrylate in different solvents (8) a dependence of the tacticity and the relative reactivity ratios on the polarity of the solvent used has been observed. We have found the same influence of the reaction medium at the copolymerization of 2-NM with St (4) and AN (5).

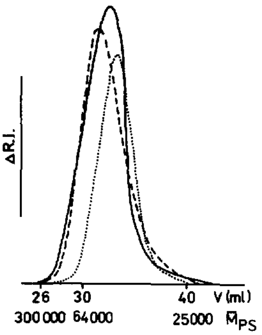
We used GPC to check the influence of the chemical nature of different solvents on the MWC of these copolymers.

The numerical data obtained for the MWC of 2-NM/St copolymers are given in Table 1 and the elution curves are shown on Figure 1. With increasing the 2-NM contents in the copolymers, independently in which solvent they are formed, the molecular weight and the polydispersity of the copolymers become higher. On the other side the copolymers formed in chloroform, benzene and 1,4-dioxane (solvents with low dielectric constants) exhibit higher molecular weights and polydispersities compared to these formed in acetone and acetonitrile (solvents

Table 1: GPC analysis of 2-NM/St copolymers formed during polymerization in different solvents

Solvent (dielectric constant)	2-NM content in the copolymer (weight %)	$\overline{M}_w$ (GPC)	$\overline{M}_w/\overline{M}_n$ (GPC)
Chloroform (4,7)	35,9	25 000	1,72
	61,6	52 000	2,28
	69,1	53 000	2,91
Benzene (2,3)	44,8	32 000	1,95
	60,6	33 000	2,36
	91,4	59 000	2,51
1,4-Dioxane (2,2)	36,8	16 000	1,68
	38,5	18 000	1,75
	73,8	51 000	2,08
Acetone (20,7)	38,6	9 000	1,54
	49,5	13 000	1,51
	77,0	28 000	1,74
Acetonitrile (36,2)	29,6	10 000	1,47
	62,3	17 000	1,67
	81,7	25 000	1,95

Figure 1: GPC chromatograms of 2-NM/St copolymers obtained by polymerization in different solvents (DRI)



——: chloroform (2-NM content 61,6 weight %)

---: benzene (2-NM content 60,6 weight %)

···: acetonitrile (2-NM content 62,3 weight %)

with high dielectric constants).

It has been shown that in chloroform there exist complexes 2-NM/2-NM whereas in solvents with high dielectric constants the free monomer molecules predominate (9). Other authors have found a relation between the formation of intermolecular complexes and the propagation of the macroradical (10). Consequently it may be assumed that the complexes mentioned may contribute for the high molecular weights obtained in non-polar solvents.

For the solution polymerization the average rate of polymerization $\overline{P}_n$ is given by the equation

$$\frac{1}{P_n} = C_M + C_S\frac{[S]}{[M]} + C_I\frac{[In]}{[M]} + \frac{K_t\,[M_n^{\bullet}]}{K_p\,[M]} \qquad (1)$$

where C_M, C_S and C_I are the chain transfer constants to the monomer, solvent and initiator; [S], [In] and [M] are the molar concentrations of the solvent, initiator and monomer; $[M_n^{\bullet}]$ is the concentration of the growing macroradicals; K_t and K_p are the chain termination and chain propagation constants. It is known that the chain transfer has the strongest influence upon the molecular weight of the polymer obtained. The chain transfer constants of AIBN and St are equal to zero (11). For C_M of 2-NM there are no data in the literature but it could be suggested that its value is close to zero, as for its structural analogue methyl methacrylate it is known to be zero (11). The data given show that C_S has the strongest influence on the MWC of the copolymers formed. As in acetone C_S is $4{,}1.10^{-4}$ (12) and in chloroform it is $0{,}5.10^{-4}$ (12), the molecular weights of the products obtained in the former solvent are lower. The polydispersity indexes are close to 1,5 indicating predominant chain termination by recombination. In the non-polar solvents, however, the majority of the $\overline{M}_w/\overline{M}_n$ values are close to 2 which means that the chain termination in these cases proceeds mainly by disproportionation.

Table 2 gives the data of the GPC analysis of 2-NM/AN copolymers formed in different solvents. The influence of the reaction medium on the MWC of the copolymers is also obvious. For copolymers with similar compositions the molecular weights obtained in chloroform and benzene are lower than in acetone and acetonitrile. With the increase of the molecular weight the polydispersity also increases.

As already pointed out C_I of AIBN is zero, C_M of AN may be neglected (13). Therefore for the system 2-NM/AN the molecular weight is predominatly affected by C_S. For chloroform, benzene and acetone the C_S values of AN are $5{,}6.10^{-4}$, $2{,}5.10^{-4}$ and $1{,}13.10^{-4}$ which could explain the changes in the molecular

Table 2: GPC analysis of 2-NM/AN copolymers formed during polymerization in different solvents

Solvent (dielectric constant)	2-NM content in the copolymer (weight %)	$\overline{M}_w$ (GPC)	$\overline{M}_w/\overline{M}_n$ (GPC)
Chloroform (4,7)	72,6	9 000	1,57
	85,2	15 000	1,76
	95,0	95 000	2,76
Benzene (2,3)	69,3	15 000	1,48
	77,2	19 000	1,75
	95,3	138 000	2,17
Acetone (20,7)	73,3	24 000	1,54
	80,3	47 000	1,58
	93,4	148 000	2,71
Acetonitrile (36,2)	69,0	20 000	1,63
	85,5	38 000	1,82
	94,9	123 000	2,08

weights with variation of the solvent. These results agree with the earlier observed alterations in the molecular weights of poly-2-NM with the change in the solvent, the highest $\bar{M}_n$ values being observed in acetone (2). Evidently the influence of the 2-NM/2-NM and 2-NM/AN complexes existing in chloroform on the molecular weights is much lower than that of the chain transfer constant C_S.

Comparing the molecular weights of the copolymers 2-NM/St and 2-NM/AN formed in chloroform (Table 3) which contain almost equal amounts of 2-NM it is seen that the copolymer 2-NM/St has higher molecular weight. As both copolymers are formed at the same reaction conditions the differences in the molecular weights could be explained with the different chemical nature of the comonomer expressed by the differences in C_M.

Table 3: GPC analysis of 2-NM copolymers formed during polymerization in chloroform

Copolymer	2-NM content in the copolymer (mol %)	$\bar{M}_w$ (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)
2-NM/AN	39,8	9 000	1,57
2-NM/St	43,9	52 000	2,28

REFERENCES

1. K. Plochocka, J.Macromol.Sci., Rev.Macromol.Chem. C 20(1), 67 (1981)
2. H. Boudevska, Ch. Brutchkov, S. Platchkova and J.P. Pascault, Makromol.Chem. 182, 3257 (1981)
3. H. Boudevska and Ch. Brutchkov, Makromol.Chem. 180, 1661 (1979)
4. H. Boudevska, O. Todorova, Ch. Brutchkov and D. Braun, Makromol.Chem., in press
5. H. Boudevska and V. Sinigersky, Makromol.Chem. 185, 531 (1984)
6. R.D. Hester and P.H. Mitchell, J.Polym.Sci., Polym.Chem.Ed. 18, 1727 (1980)
7. H. Boudevska, Ch. Brutchkov, V. Koleva and Q.T. Pham, Eur. Polym.J. 14, 619 (1978)
8. H. Boudevska, Ch. Brutchkov and V. Veltchev, Eur.Polym.J. 15, 907 (1979)
9. H. Boudevska, Ch. Brutchkov and V. Koleva, Makromol.Chem. 179, 2031 (1978)
10. P. Hyde and A. Ledwith in "Molecular Complexes", ed. by R. Foster, Eleck Science London, 173 (1974)
11. G. Odian, "Principles of Polymerization", Russ.Ed., Mir Moscow, 192 (1974)
12. I. Panayotov, S. Fakirov, "Polymer Chemistry and Physics", Nauka i Iskoustvo Sofia, 81 (1982)
13. G. Ham,' "Copolymerization", Russ.Ed., Mir Moscow, 365 (1971)

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