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## ROLE OF SOLVENT IN THE HETEROPHASE COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH VINYL ISOBUTYL ETHER

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### ABSTRACT

The aim of our investigation was to find out to what extent benzene (B) could be replaced by less toxic solvents like toluene (T) and ethylbenzene (EtB) in an alternating heterophase copolymerization of maleic anhydride (MAn) with vinyl isobutyl ether (ViBE). Low yields excluded copolymers obtained by the use of EtB. The investigations were designed to establish relations between initiator (benzoyl peroxide) concentrations and such parameters as weight-average molecular weights ( $\overline{M}_w$ ), intrinsic viscosities ( $[\eta]$ ), sedimentation constants ( $s_0$ ), and degrees of conversion ( $\alpha$ ). By raising the initiator concentration in benzene from 0.00 to 0.20 mol% after 4 hours of polymerization at 60°C, an increase of  $\overline{M}_w$  from  $29 \times 10^3$  to  $850 \times 10^3$  g/mol was found. Parallel to that, the degree of conversion went from 12% up to 98%. In toluene, on the other hand, the corresponding increase of  $\overline{M}_w$  was from  $80 \times 10^3$  to  $290 \times 10^3$  g/mol only, whereas the degrees of conversion were 61% and 81%. The intrinsic viscosities ( $[\eta]$ ) and sedimentation constants ( $s_0$ ) gave rise to the following correlations:

$$[\eta] = 1.16 \times 10^{-4} \overline{M}_w^{0.705}$$
$$s_0 = 6.87 \times 10^{-17} \overline{M}_w^{0.752}$$

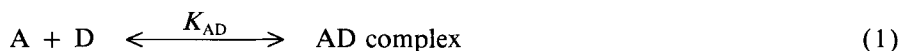
The structure of poly(MAn-co-ViBE) was elucidated by  $^{13}\text{C}$ -NMR spectroscopy.

## INTRODUCTION

In view of the many restrictions put on solvents used in industry, it seems desirable to replace benzene by a less dangerous hydrocarbon. Such a problem exists when maleic anhydride, MAn, is submitted to alternating copolymerizations with appropriate electron-donating comonomers via a solution-precipitation polyreaction. An advantage of heterophase polymerization results from the copolymer being a powder, which in many cases is very desirable compared to the use of benzene in large-scale processes. However, there are only few less volatile organic solvents which are suitable for replacing benzene in large-scale processes involving solution-precipitation polymerizations. Among such solvents, toluene and ethylbenzene can be considered.

The aim of the present work was therefore to compare how copolymerization of MAn with vinyl isobutyl ether (ViBE) proceeds in benzene (B), toluene (T), and ethylbenzene (EtB), respectively (see page 75).

The alternating character of the MAn/ViBE copolymer is rooted in the  $Q, e$  values, which for MAn are  $Q_1 = 0.23$ ;  $e_1 = 2.25$ , and for ViBE are  $Q_2 = 0.023$ ;  $e_2 = -1.77$  [1]. The large  $\Delta e$  value (4.02) indicates a strong tendency to form electron acceptor-donor complexes [2] according to



where A stands for the acceptor (MAn) and D for the donor (ViBE) comonomer.

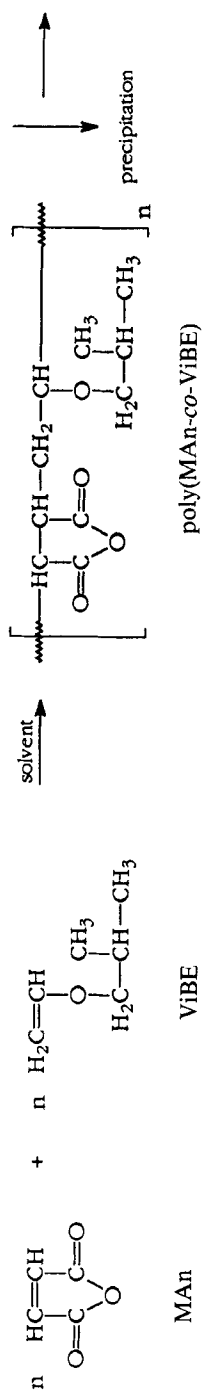
Due to the equilibrium state shown in Eq. (1), the kind of solvent should influence the equilibrium constant  $K_{AD}$ . Polar solvents will shift the equilibrium more to the left, whereas nonpolar solvents will cause a shift to the right. Whether a left shift or a right shift is more favorable depends on the mechanism of alternating copolymer formation. According to Iwatsuki and Yamashita [3], only AD complexes should be regarded as the reactive units taking part in the propagation step. On the other hand, however, Georgiev et al. [4] found the A and D monoradicals to be the reactive centers when tracing the sequence of elementary reactions by means of ESR measurements. Keeping in mind that toluene and ethylbenzene are somewhat polar whereas benzene is nonpolar, benzene should be a better solvent if the first concept is true, while toluene and ethylbenzene should display properties superior to benzene if the second notion is true.

A further aim was to check the structure of the poly(MAn-co-ViBE) obtained, and to develop the conditions needed to tailor the average molecular masses,  $\bar{M}$ , of the copolymers resulting from a heterophase process. Molecular masses are decisive for determining the applicability of this copolymer in many fields.

## EXPERIMENTAL

### Materials

Maleic anhydride and benzoyl peroxide, both from Sojuzchim, USSR, reagent grades, were recrystallized from chloroform and vacuum dried. Vinyl isobutyl ether (ViBE) from Light Labor Ltd., England, reagent grade, was agitated with a 5%  $\text{Na}_2\text{SO}_4$  solution for the purpose of removing traces of peroxides, after which it was



kept for 7 days over activated zeolite A-4 and distilled at 82°C. The purity was checked refractometrically. All solvents were dried just before use and distilled. Thus, dimethylformamide (DMF), from POCh Gliwice, Poland, was dried with calcium chloride and distilled under nitrogen at a reduced pressure (38 mmHg) at 65°C; benzene (B), toluene (T), ethylbenzene (EtB), and chloroform, all from POCh Gliwice, Poland, were dried for 7 days over activated zeolite A-4 and then distilled. Prior to application, solvents were tested for the absence of water by IR spectroscopy.

## Procedure

Copolymers, poly(MAN-*co*-ViBE), were prepared by dissolving 5.94 g (0.06 mol) of MAN in 30 cm<sup>3</sup> of one of the three solvents (benzene, toluene, ethylbenzene) and then a given amount (or nothing) of benzoyl peroxide was added (0.02, 0.05, 0.1, or 0.2 mol%). The solution was transferred into a vial (100 cm<sup>3</sup>) and mixed with 6 g (0.06 mole) of ViBE. The vial was sealed and warmed at 60°C for 4 hours after its content had been flushed with purified nitrogen. In cases without initiator, the polymerization time was prolonged to 27.5 hours. All copolymers yielded a dispersed phase which settled and could be separated. The powders were withdrawn quantitatively, rinsed with chloroform, vacuum dried, and weighed in order to determine the degree of conversion. Samples designed for measurements were purified by alternatively dissolving in DMF and precipitating with chloroform.

## Measurements

Viscometric determinations were carried out with dilution of the same sample using an Ubbelohde viscometer. Its capillary was matched for requirements of neglecting the Hagenbach correction. For five concentrations in the range from 0.25 to 0.50 g/100 cm<sup>3</sup>, reduced specific viscosities  $\eta_{sp}/c$  were established and extrapolated to zero concentration. The intrinsic viscosities were calculated by means of the least-squares method. All measurements were carried out at 25 ± 0.01°C in DMF as solvent.

Molecular weight determinations were carried out at 25 ± 0.02°C in a photodiffusogoniometer Sofica-type 1200 in five solutions in DMF of each of the copolymers investigated, comprising the concentration range  $c = 0.5$  to 1.0 g/100 cm<sup>3</sup>. The refractive increment  $dn/dc = 0.8411$  was determined by the use of a differential spectrometer Zeiss Jena type PR-2.

Sedimentation constants ( $s_0$ ) were determined at 20°C by using an analytical ultracentrifuge MOM 3180 employing 36,000 rpm. For five concentrations, photographs were made at constant time intervals, and the sedimentation coefficient  $s$  was calculated according to Elias [5]. By extrapolating the  $s$  value to zero concentration, the sedimentation constant  $s_0$  was determined.

The <sup>13</sup>C-NMR spectrum was recorded on a Varian VXR 300 spectrometer using the following set of conditions: pulse width, 8.7 μs (25°C); spectral width, 17,605.6 Hz; acquisition time, 1.194 seconds; transients, 3000; solvent, 15 wt% NaOH in D<sub>2</sub>O estimated; internal reference, TMS.

## RESULTS, DISCUSSION, AND CONCLUSIONS

The heterophase radical copolymerization of MAN with ViBE afforded alternating copolymers poly(MAN-co-ViBE), designated additionally by the letters B, T, and EtB to indicate the solvent used. A further designation by consecutive numerals 0.00, 0.02, 0.05, 0.10, and 0.20, refers to initiator concentrations employed in the 16 polyreactions carried out according to data presented in Table 1.

The temperature of copolymerization was kept constant at 60°C, and the time was varied from 4 to 20 hours, with 4 hours being the usual time.

As can be seen from Table 1, the kind of solvent exerts a substantial influence on the degree of conversion  $\alpha$ . In benzene the yields are about 95%, whereas in toluene their values range between 70 and 80%. The yields are still less in ethylbenzene (30%). The reason may be a chain transfer to solvent [6] that makes ethylbenzene best suited for the preparation of MAN/ViBE oligomers, which are applicable for some usages. The preparation of these oligomers will be the subject of a separate paper.

Due to the chain transfer effect, there were grounds to expect smaller molecular weights in toluene compared to benzene. In fact, the respective weight-average molecular weights  $\bar{M}_w$ , are smaller in toluene, as shown in Table 1. The appropriate

TABLE 1. Variations of Degrees of Conversion  $\alpha$ , Intrinsic Viscosities  $[\eta]$ , Sedimentation Constants  $s_0$ , Weight-Average Molecular Masses  $\bar{M}_w$  in the Products Obtained after Time  $\tau$  by Heterophase Copolymerization of Maleic Anhydride (MAN) with Vinyl Isobutyl Ether (ViBE) in Benzene (B), Toluene (T), or Ethylbenzene (EtB)

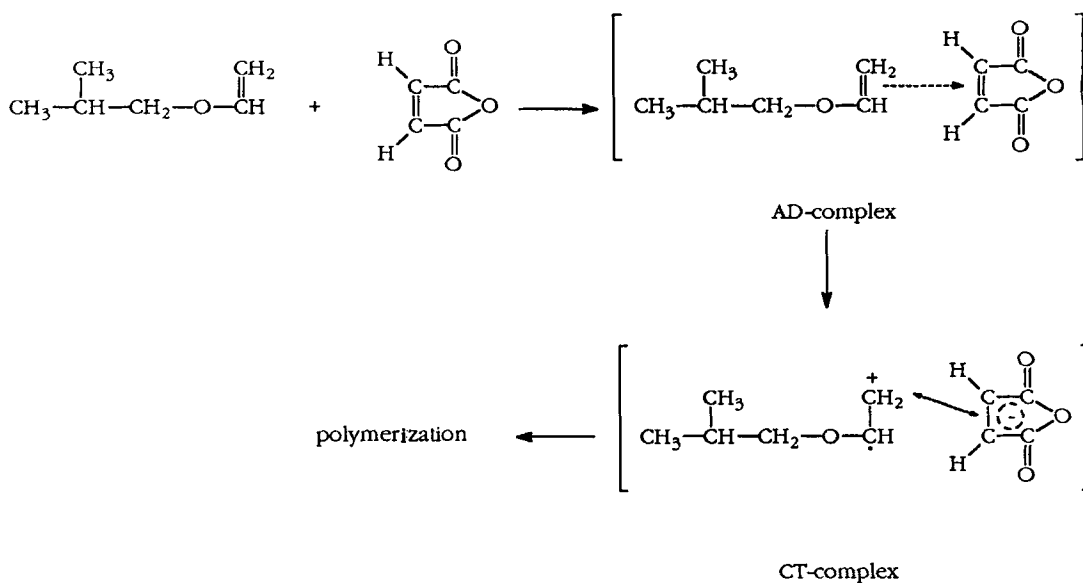
Sample [(copolymer) solvent/initial concentration in mol%]	$\tau$ , h	Degree of conversion, $\alpha$ , %	$[\eta]$ , 100 cm <sup>3</sup> /g	$s_0 \times 10^{13}$ , s <sup>-1</sup>	$\bar{M}_w \times 10^{-3}$ , g/mol
Poly(MAN-co-ViBE)B/0.00*	28.0	69.4	0.932	10.18	345.0
Poly(MAN-co-ViBE)B/0.00	4.0	12.3	0.164	1.57	29.2
Poly(MAN-co-ViBE)B/0.02	4.0	95-98	1.266	14.21	529.7
Poly(MAN-co-ViBE)B/0.05	4.0		1.225	13.17	511.1
Poly(MAN-co-ViBE)B/0.10	4.0		1.653	18.43	776.1
Poly(MAN-co-ViBE)B/0.20	4.0		1.763	20.02	850.6
Poly(MAN-co-ViBE)T/0.00	27.5		75.4	0.359	3.57
Poly(MAN-co-ViBE)T/0.02	5.5	72.7	0.334	3.45	80.5
Poly(MAN-co-ViBE)T/0.05	4.0	61.1	0.448	4.50	122.0
Poly(MAN-co-ViBE)T/0.10	4.0	75.7	0.611	6.67	190.0
Poly(MAN-co-ViBE)T/0.20	4.0	80.6	0.822	8.70	289.0
Poly(MAN-co-ViBE)EtB/0.00	27.5	< 50			
Poly(MAN-co-ViBE)EtB/0.02	9.0				
Poly(MAN-co-ViBE)EtB/0.05	4.0				
Poly(MAN-co-ViBE)EtB/0.10	4.0				
Poly(MAN-co-ViBE)EtB/0.20	4.0				

values of the intrinsic viscosities ( $[\eta]$ ) and sedimentation constants ( $s_0$ ) are smaller too. Thus, an increase in initiator concentration from 0.02 to 0.20 mol%, at constant  $\tau$  (4 hours), causes the  $\overline{M}_w$  values to grow from 29,000 to 850,600 g/mol in benzene, and only from 89,000 to 289,000 g/mol in toluene, in which the growth is significantly smaller. The proportional relationship between initiator concentration and degree of polymerization results from the specificity of heterophase polymerization.

Note that the polyreaction proceeds even without the use of any initiator, but in such cases the time needed to achieve a reasonable output is much longer. This is evident by comparing poly(MAn-co-ViBE)B/0.00 to poly(MAn-co-ViBE)B/0.00\* (see Table 1).

In toluene the yields, which are generally smaller, are associated with a smaller average molecular weight. This finding may partly be attributed to the peculiarity of heterophase polymerization and partly to the occurrence of chain transfer to solvents. As a rule, the relationships resulting from heterophase systems differ from those found in homogenous solutions.

The fact that MAn/ViBE copolymerization can be started without an initiator indicates that the charge transfer AD complexes are reactive centers, the formation of which can be explained as follows:



The electron-donating capacity of ViBE is evidently high enough ( $\Delta e = 4.02$ ) to bring about the above complexation.

The relationships of  $\eta_{sp}$  vs  $c$  and of  $s$  vs  $c$  yielded intrinsic viscosities ( $[\eta]$ ) and sedimentation constants ( $s_0$ ). These parameters, which are related to the appropriate weight-average molecular weights, afforded double logarithmic correspondences from which the following equations could be established:

$$[\eta] = 1.16 \times 10^{-4} \overline{M}_w^{0.705} \quad (2)$$

$$s_0 = 6.87 \times 10^{-17} \overline{M}_w^{0.752} \quad (3)$$

The  $^{13}\text{C}$ -NMR spectrum is shown by Fig. 1 for poly(MAn-co-ViBE)B/0.02.

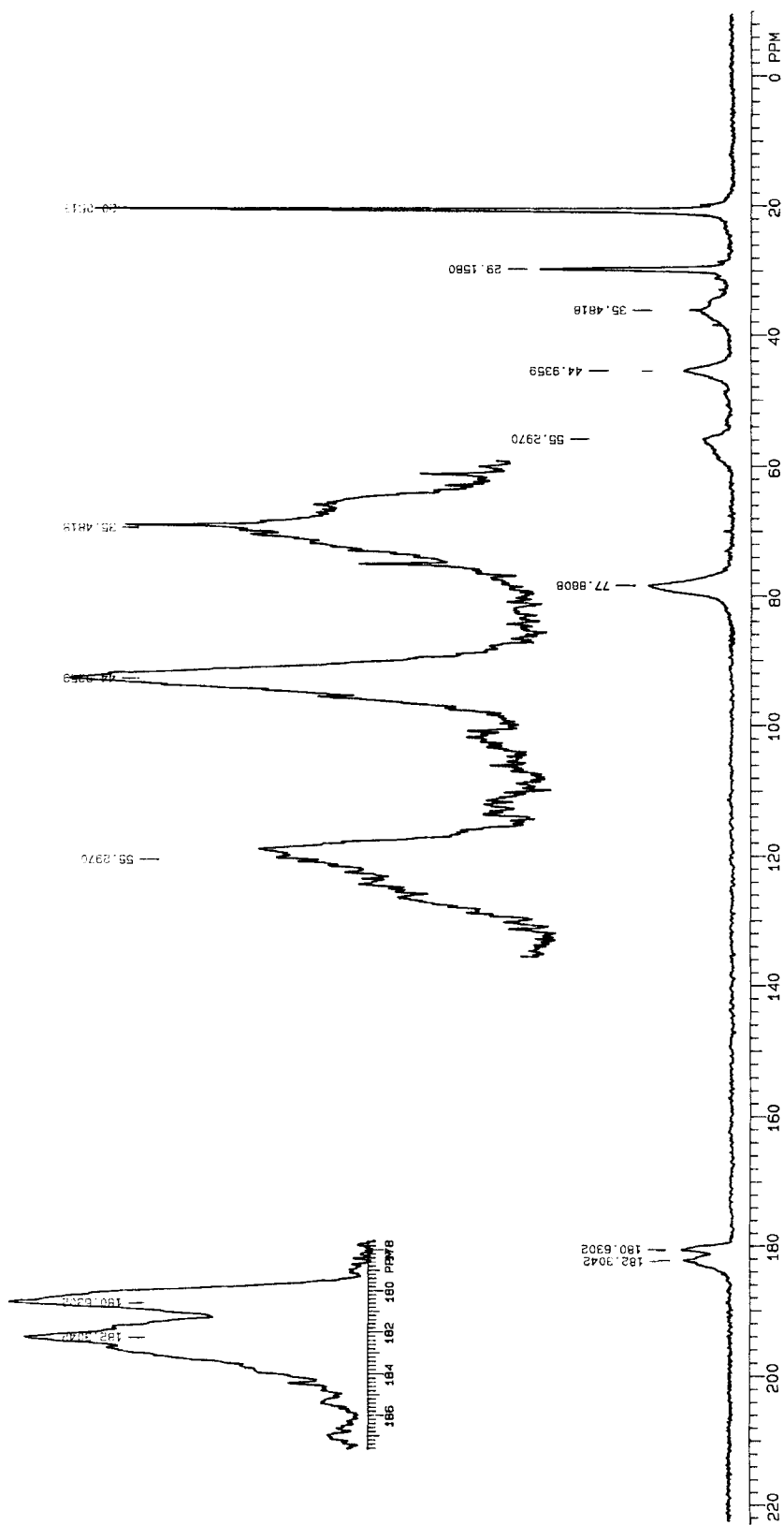
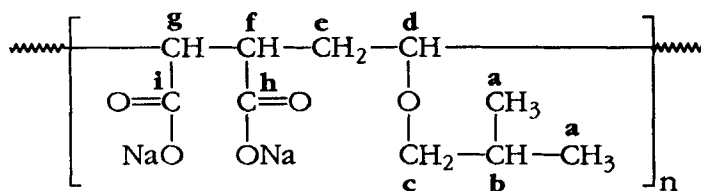


FIG. 1. <sup>13</sup>C-NMR spectrum of poly(MAN-co-ViBE)B/0.02, where MAN = maleic anhydride, ViBE = vinyl isobutyl ether, B = benzene (solvent used), and 0.02 denotes the concentration of benzoyl peroxide applied as initiator in the polymerization.



Each peak in the  $^{13}\text{C}$ -NMR spectrum is designated by a consecutive number 1, 2, 3, . . . (from high to low field).

The assignment of the peaks to individual structural C atoms was based on the works of Koenig [6], Rätzsch et al. [7], and our own two papers [8]. Carbons belonging to the repeating unit of the copolymer were labeled by the consecutive letters **a**, **b**, **c**, . . . , **i**. Values of the chemical shifts represented in the  $^{13}\text{C}$ -NMR spectrum (see Fig. 1) were ascribed to the corresponding C atoms of the repeating unit as follows:



poly(MAN-co-ViBE) hydrolyzed

Peak	C atom	Peak form	Assignment ( $\delta$ in ppm)
1	<b>a</b>	Singlet	20.05
2	<b>b</b>	Singlet	29.15
3	<b>e</b>	Broad	35.48
4	<b>f</b>	Broad	44.94
5	<b>g</b>	Broad	55.29
6	<b>c, d</b>	Broad	77.87
7	<b>h</b>	Broad	180.63
8	<b>i</b>	Broad	182.31

Because of the polymeric nature of poly(MAN-co-ViBE), a satisfactory NMR solvent could not be found that would provide a high concentration of the copolymer, which therefore was hydrolyzed by the use of an aqueous 2 N NaOH solution.

In analyzing the spectrum shown in Fig. 1, the point to remember is that the C atoms **f** and **g** give rise to *threo* (*trans*) and *erythro* (*cis*) isomerism. As a consequence of overlapping of the respective enantiomeric doublets, broad signals appear. On the other hand, the signals of the two carbonyl carbons are distinctive, which results from the influence of the side group in the vinyl ether unit.

Different  $^{13}\text{C}$ -NMR spectra, however, are evidenced by the low molecular weight MAN/ViBE copolymers obtained in ethylbenzene with benzoyl peroxide as initiator. The reason for the deviations will be explained in a separate paper.

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