

# Porous Maleic Anhydride–Styrene–Divinylbenzene Copolymer Beads

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## Synopsis

The formation of the porosity and the pore stability in maleic anhydride–styrene–divinylbenzene (MAN–St–DVB) copolymer beads were investigated using the apparent density measurements of the samples dried from methanol (maximum porosity) and from dioxane (stable porosity). The copolymer beads were prepared by the suspension polymerization method in glycerol instead of water as the dispersing medium. A toluene–dioxane (1 : 1) mixture was used as the diluent at a fixed volume fraction of the organic phase (0.47). Compared to St–DVB copolymers prepared in the presence of nonsolvating diluents, porous MAN–St–DVB copolymers are obtained at relatively low DVB concentration, i.e., at 1–3% DVB. The porosity of the copolymers increases with decreasing MAN concentration in the feed due to the decrease in the copolymer yield. The results of the elemental analyses and titrimetric methods indicate that approximately only half of the MAN units in the copolymer are able to react with amine or with water. A possible rearrangement of the MAN units into the cyclopentanone structures was suggested.

## INTRODUCTION

Maleic anhydride–styrene (MAN–St) copolymers are used as starting material for many derivatives.<sup>1–3</sup> Recently, Ogawa and co-workers described the preparation of porous maleic anhydride–styrene–divinylbenzene (MAN–St–DVB) copolymer beads by suspension polymerization.<sup>4</sup> Porous copolymers have a wide range of application, such as in waste water treatment, organic synthesis, and analytical chemistry. Porous MAN–St–DVB copolymer beads are also useful in the preparation of ion exchangers.

In the present work, a number of porous MAN–St–DVB copolymers with various concentrations of MAN and DVB were prepared. A mixture of dioxane and toluene in a volume ratio 1 : 1 was used as the diluent at a fixed volume fraction of the organic phase (0.47). The pore structure of the copolymers was investigated using the apparent density measurements of the samples in the dried state. It is known that the drying process of the copolymers swollen in good solvents may lead to a partial or total collapse of the pores.<sup>5–6</sup> The preservation of the swollen state porosity (maximum porosity) in the dried state can be attained during the treatment of swollen copolymers with solvents with decreasing solvating power, before the drying process.<sup>6–8</sup> In this study, the stable part of the porosity and the maximum porosity of the copolymer samples were determined after drying the networks from dioxane and from methanol, respectively. This paper describes the conditions of the

porosity formation and pore stability in the MAn–St–DVB copolymers. The copolymer composition in relation to the synthesis conditions is also described.

## EXPERIMENTAL

### Materials

The commercial St and DVB were purified and distilled in the usual way. The composition of DVB, as determined by G.C., was 60% DVB isomers (*m*-DVB : *p*-DVB ratio 1.6), 37% ethylvinylbenzene and nonpolymerizable compounds. Dibenzoyl peroxide (Merck, West Germany) was dried prior to use. All the solvents and reagents were of reagent grade and were used as received. Glycerol (United Chem. Co., Turkey) contained 0.5–0.7% water. MAn was of chemical grade (purity > 99%).

### Copolymerization

The MAn–St–DVB copolymers were obtained by the suspension polymerization method. Glycerol was used as the dispersing medium instead of water to protect the anhydride groups.<sup>4</sup> A mixture of dioxane and toluene was used as the diluent at a fixed volume ratio (1 : 1). The volume fraction of the diluent in the organic phase was constant at 0.47 throughout the study, and only the DVB and MAn concentrations were varied.

Copolymerization was conducted in a 500-mL round bottom, four-neck flask, fitted with a mechanical stirrer, nitrogen inlet, condenser, and pipette outlet. All reactions were carried out at  $70 \pm 0.5^\circ\text{C}$ . A mixture of 135 mL of glycerol containing hydroxyethyl cellulose Natrosol-HR (0.6 g) and sodium chloride (7.0 g) was first introduced into the reactor and stirred at 200 rpm at room temperature for 1 h. The suspending medium was then heated to the reaction temperature. A mixture of the monomers (34 mL), dioxane (15 mL) and toluene (15 mL), containing dibenzoyl peroxide as the initiator (2.14 wt % in relation to the monomers) was added to the reactor and the reaction was allowed to proceed for 2 h. After polymerization, the copolymer beads of 0.35–1.0 mm in diameter were first washed with water and then with acetone; finally they were swollen to equilibrium in dioxane at room temperature. A part of the swollen copolymers was dried *in vacuo* at room temperature whereas another part was successively washed with solutions whose compositions were changed gradually from dioxane to pure methanol. The samples after treatment with methanol as a final solvent were dried *in vacuo* at room temperature.

It must be pointed out that the MAn–St–DVB copolymers undergo the typical reactions of anhydrides with amines, alcohols, and water. Ogawa et al. have reported that the MAn solution in glycerol is expected to be stable for hydrolysis and production of polyester unless the temperature is too high.<sup>4</sup> They also reported that the final beads contained 7% of free carboxyl groups. The copolymer composition may also be affected by the methanol and water used in the post-treatment of the samples during the present study.

### Methods

The apparent density of the copolymers,  $d_0$ , was determined by the mercury pycnometric method.<sup>9</sup> Porosity,  $P\%$ , was calculated from  $d_0$  as

$$P\% = (1 - d_0/d_2) \times 100\% \quad (1)$$

where  $d_2$  is the density of homogeneous MAN-St-DVB copolymers. The values of  $d_2$  for all the copolymer samples were taken as 1.08 g/cm<sup>3</sup>, which is the density of homogeneous St-DVB copolymers.

The volume swelling ratio  $q_v$  was determined by placing the copolymer beads dried from methanol in a graduated cylinder and reading the volume. An excess of dioxane as the swelling agent was then added, and the volume was read at the swelling equilibrium.  $q_v$  was calculated as

$$q_v = \text{final volume}/\text{initial volume} \quad (2)$$

The anhydride group content of the copolymers was determined by the method given by Johnson and Funk.<sup>10</sup> The method is based on the reaction of the anhydride groups with morpholine and titration of excess morpholine with 0.2N perchloric acid in acetic acid. The total amount of anhydride and free carboxyl groups were determined as follows: About 200 mg of the copolymer was hydrolyzed in 25 mL 0.1N NaOH at 90°C for 3 h. After cooling, the mixture was transferred into a beaker with 20 mL of water, and titrated with 0.1N methanolic HCl using phenolphthalein.

The infrared spectra of the copolymers in KBr pellets were recorded on a Perkin-Elmer 983 spectrophotometer. C and H analyses of the selected samples were performed on a Perkin-Elmer 240 C elemental analyzer.

### Reaction with *N*-(Diethylaminopropyl)amine

The aminated products were prepared by adding a solution of *N*-(diethylaminopropyl)amine (2 g; 15 mmol) in dioxane (5 mL) to 5 g of the copolymer beads swollen to equilibrium in 40 mL of dioxane, and heating the mixture at 80°C for 3 h. The reaction mixture was then cooled and washed with dioxane and finally with diethyl ether. The copolymer was then dried *in vacuo* at room temperature.

## RESULTS AND DISCUSSION

Previous studies on the heterogeneous polymerization of MAN-St-DVB show that the copolymerization rapidly proceeds up to the maximum value in about 2 h, and then levels off.<sup>11,12</sup> The abrupt increase in the polymerization rate at the earlier stage shows the autoacceleration effect of heterogeneous polymerization.

A series of experiments were carried out at 60 mol % MAN and 10.5 mol % DVB in the feed, to find the optimum polymerization time to reach maximum conversion. It was found that the copolymer yield did not change between 1 and 4 h, and remains at about 40%.

TABLE I  
Composition of the Monomer Mixtures and the Properties of the Resulting Copolymers<sup>a</sup>

Series	Sample no.	MAn (mol %)	DVB (mol %)	$d_0$ (g/cm <sup>3</sup> )		P%	
				D	M	D	M
I	1	60	0.3	1.2	1.09	0	0
	2	60	0.6	1.2	0.98	0	9
	3	60	1.1	1.2	0.71	0	34
	4	60	2.0	0.71	0.57	34	47
	5	60	3.4	0.61	0.53	43	51
	6	60	6.9	0.58	0.55	46	49
	7	60	10.5	0.61	0.59	44	46
II	8	40	0.4	1.2	0.49	0	55
	9	40	0.6	1.2	0.41	0	62
	10	40	0.9	1.2	0.52	0	52
	11	40	1.2	1.2	0.38	0	65
	12	40	1.8	1.2	0.48	0	56
	13	40	2.4	1.2	0.57	0	47
	14	40	3.7	0.97	0.60	10	45
	15	40	6.2	0.95	0.76	12	30
	16	40	10.0	1.07	0.90	0	15
III	17	20	4.0	0.98	0.63	9	42
	18	20	6.8	1.08	0.84	0	23
	19	20	12.4	1.00	0.96	7	11

<sup>a</sup> $d_0$  = apparent density and P% = total porosity of copolymers dried from dioxane (D) and from methanol (M).

### Porosity Formation

There are three main parameters for the preparation of a porous copolymer<sup>13</sup>:

- (1) the crosslinking agent concentration in the monomer mixture,
- (2) the volume of the diluent, and
- (3) the type of the diluent.

In this study, the parameters (2) and (3) were kept constant, whereas only the first parameter was varied at a given MAn concentration. The composition of the starting monomer mixtures and the properties of the copolymer samples are listed in Table I. In series I, i.e., for 60 mol % MAn in the feed, the porosity of the copolymers dried from methanol, i.e., the maximum porosity increases linearly with increasing DVB concentration up to approximately 3% (Table I and Fig. 1). The maximum porosity decreases slightly with a further increase in the DVB concentration. At 10.5% DVB, the experiments were carried out at different polymerization time to find the change in the porosity during the course of the polymerization. As seen in Figure 2, the porosity decreases with increasing time of polymerization. The result suggests that the decrease in the porosity above 3% DVB is due to the destruction of the rigid pore structure during the polymerization or during the measurements.

For smaller DVB concentrations, the pore structure of the copolymers is not stable and collapses totally on drying in the swollen state (Fig. 1). Similar

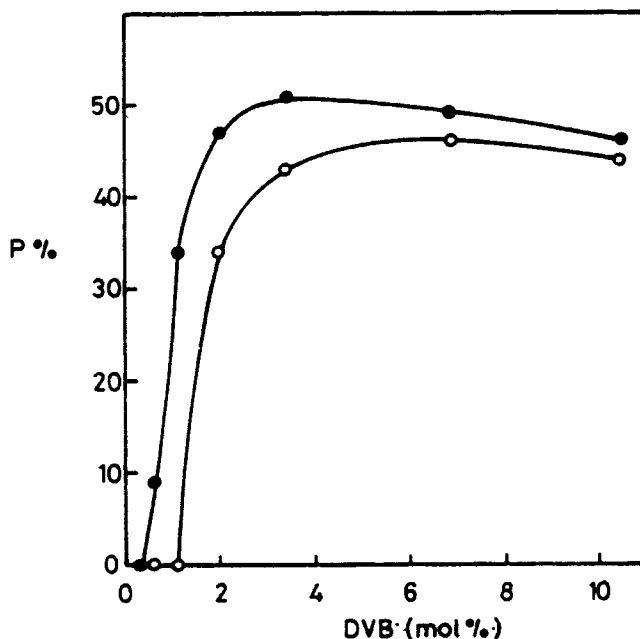


Fig. 1. Dependence of the total porosity  $P\%$  on the DVB concentration for copolymers from series I dried from methanol (●) and from dioxane (○).

results were found previously for St-DVB copolymers.<sup>7</sup> The swelling ratio of copolymers in series I is given in Figure 3 as a function of the DVB concentration. The degree of swelling exhibits the expected dependence on the DVB concentration and the copolymers with 1% DVB or below swell significantly. In such samples with a very low degree of crosslinking, the connection between the microgel particles must be weak,<sup>14</sup> and, thus, the pore structure formed must be loose. Most probably, the destruction of weak matrices of these samples takes place during drying in the swollen state, resulting in the disappearance of the pores in the network. From 1 to 3% DVB, the amount of

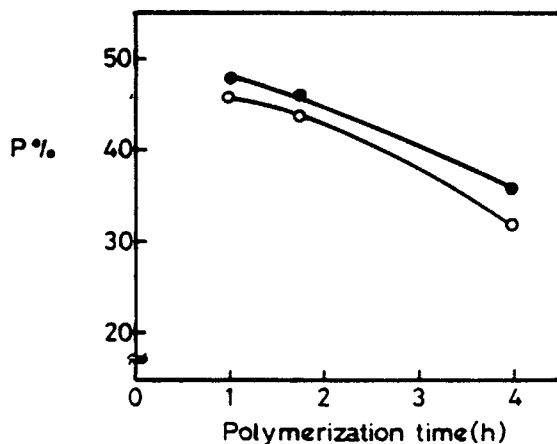


Fig. 2. Dependence of the total porosity  $P\%$  on the polymerization time for sample 7 (see Fig. 1 caption).

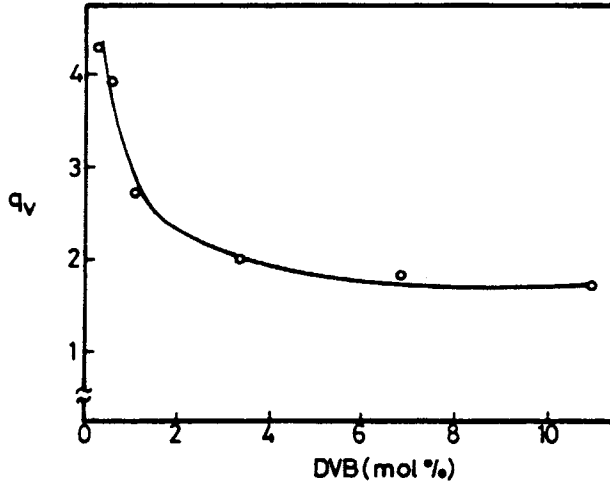


Fig. 3. Dependence of the volume swelling ratio  $q_v$  on the DVB concentration for copolymers from series I.

stable porosity increases drastically and reaches approximately the value of the maximum porosity.

For 40 mol % MAN in the starting monomer mixture, the maximum porosity increases abruptly and approaches to 65% at 1.2% DVB (Table I and Fig. 4). It seems that the phase separation occurs earlier than in the previous case and the value of the total porosity is higher than that calculated from the volume of the diluent present during the network formation.

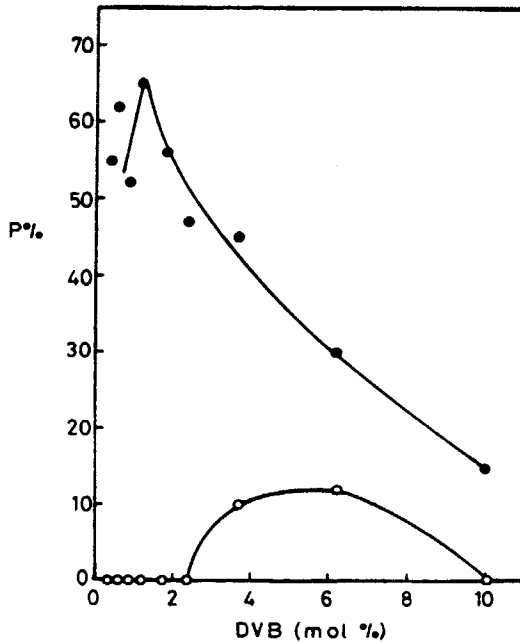


Fig. 4. Dependence of the total porosity  $P\%$  on the DVB concentration for copolymers from series II dried from methanol (●) and from dioxane (○).

As the MAN concentration decreases in the feed, the copolymer yield also decreases, and, in the presence of 20% MAN with < 4% DVB, or in the absence of MAN on the whole DVB range, no beads were obtained under the experimental conditions. The decrease in the copolymer yield corresponds to an increase in the total volume of the diluent plus the unreacted monomers in the organic phase. Thus, with decreasing MAN concentration in the feed, the parameter (2) for the porosity formation changes (increases), and propagating copolymer separates out of the monomer mixture earlier. Accordingly, the copolymers in series II show higher values for the porosity and lower values for the critical DVB concentration than in series I.

As seen from Table I, the pores of the copolymers in series II and III are mostly unstable. This situation can be explained with the thermal properties of MAN-St-DVB copolymers. The glass transition temperatures of MAN-St copolymers,  $T_g$ , increase with increasing MAN unit content of copolymers.  $T_g$  also increases with increasing DVB concentration. Recently, it was reported that  $T_g$  increases 1.48°C for each additional MAN%.<sup>15</sup> For instance, copolymers with 50% MAN pass into the rubbery state at 174°C, whereas with 40% MAN at 159°C and with 20% MAN at 130°C. Since MAN unit content of the copolymers decreases by transition from series I to series II or III,  $T_g$  of the copolymers also decreases, so that the copolymers in series II or III swollen in dioxane pass into the glassy state at higher DVB concentration than in series I. Therefore, the pores of such copolymers are expected to be stable at higher DVB concentration than those in series I. However, due to the rigidity of the copolymer structure at higher DVB concentrations, a destruction of the pore structure takes place during reactions or during measurements. As a consequence, the pore structure of copolymers in series II and III cannot be stable over the whole DVB range.

It must be pointed out that the porosity data given in this study was calculated from the apparent density of the samples using eq. (1). The density of homogeneous MAN-St-DVB copolymers was assumed to be 1.08 g/cm<sup>3</sup>. However, due to the variable composition of the MAN-St-DVB copolymers, the true porosity values may somewhat differ from those given in Table I. But, as only the apparent density values within each series of same MAN concentration are compared, deviation from the true density does not affect the results about the porosity formation and the pore stability.

### Copolymer Composition

The results of the quantitative chemical analyses of the copolymers are given in Table II. There is a gradual decrease in the oxygen content and increase in carbon and hydrogen content of the copolymer with an increase in the molar concentration of MAN or DVB in the monomer mixture. The MAN unit contents of the copolymers were calculated from the elemental analyses and are shown in the final column of Table II.

It is known that the copolymerization of MAN with St leads to copolymers with nearly equimolar ratio of monomer units, regardless of the initial ratio of the monomers. It was also reported that the copolymerization proceeds through the formation of a MAN-St complex which participates in the copolymerization.<sup>16,17</sup> The results for the copolymers in series I are in accor-

TABLE II  
 Composition and the Calculated MAn Unit Content of the Copolymers

Series	Sample no.	DVB (mol %)	C	(wt %)			(MAn) calcd (mol %)
				H	O		
I	1	0.3	70.21	6.06	23.73	50	
	2	0.6	70.14	5.80	24.06	50	
	3	1.1	70.83	5.55	23.62	50	
	5	3.4	72.16	5.59	22.25	47	
	6	6.9	73.06	5.89	21.05	45	
	7	10.5	73.65	6.01	20.34	44	
	II	11	1.2	73.92	5.78	20.30	43
14		3.7	76.81	6.56	16.63	36	
15		6.2	78.14	6.68	15.18	33	
16		10.0	79.46	7.23	13.31	29	
III	17	4.0	82.88	7.32	8.47	18	
	18	6.8	81.89	7.10	9.45	21	
	19	12.4	84.87	7.51	5.95	13	

dance with the reported data. MAn is copolymerized with St in 1:1 molar ratio. Thus, an increase in the DVB concentration leads to a decrease in the MAn unit contents of the copolymers, as seen in Table II. However, the decrease in the MAn concentration in the feed resulted in the smaller MAn unit contents. In addition, at a given MAn concentration, the MAn unit content decreases further with increasing DVB concentration. Similar results were obtained by Mizutani and Matsuoka for MAn-St-DVB copolymerization in kerosene.<sup>12</sup> The increase in the amount of DVB promotes the formation of crosslinked copolymers and increases the copolymer yield. Since MAn is copolymerized more rapidly than the other monomers,<sup>17</sup> the increase in the yield at a given MAn concentration necessarily decreases the MAn unit content of the copolymers.

The content of free carboxyl groups in hydrolyzed copolymers and the corresponding MAn unit contents are given in Table III. The results of the anhydride group determination by the morpholine method gave approximately the same values, as seen in the final column of Table III. No hydrolysis can be detected with the methods used. The results of the MAn

 TABLE III  
 MAn Unit Content of the Copolymers Analyzed by the Titration Methods

Series	-COOH (mmol/g)	MAn (mol %)	
			<sup>b</sup>
I	5.0-6.0	25-30	24-29
II	2.4-3.4	13-17	10-15
III	0.4-1.4	2-7	4-9

<sup>a</sup> Calculated from the free carboxyl groups in hydrolyzed copolymers given in the first column of the table.

<sup>b</sup> Found by the morpholine method.



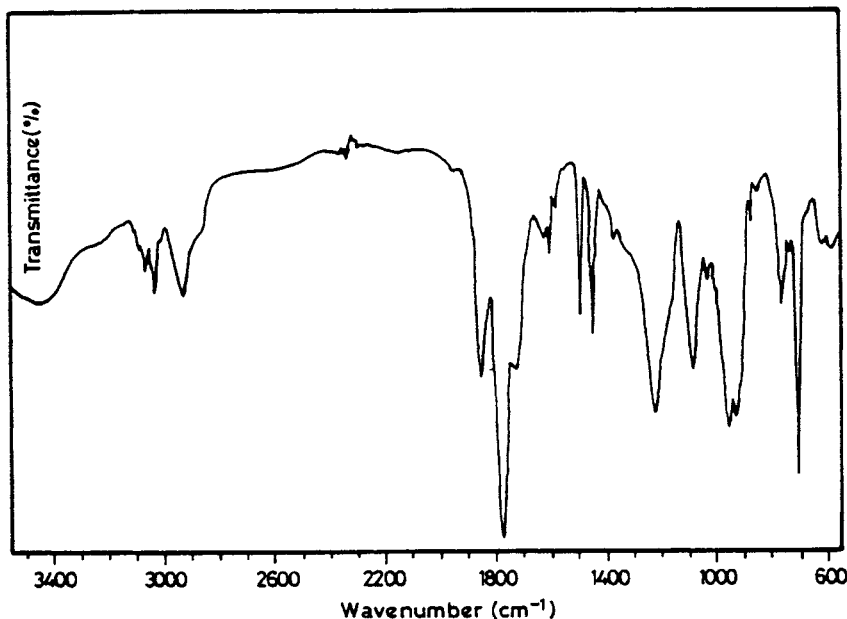


Fig. 5. IR spectrum of sample 11 in KBr pellet.

unit content of the copolymers in series I are in accordance with the data given by Ogawa et al.<sup>4</sup> They found 2.6 mmol/g MAN unit in the copolymer (2.5–3.0 mmol/g in this work). It is surprising that only half of the MAN units calculated from the elemental analyses can be detected titrimetrically. Infrared spectra of the copolymers from series I to III were taken; a typical spectrum is shown in Figure 5. In all the spectra, the characteristic absorption peaks at  $1760\text{ cm}^{-1}$  due to C=O stretching from MAN and at  $1600\text{ cm}^{-1}$  due to styrene were present. As the concentration of MAN decreased in the starting monomer mixture, the absorption peak due to MAN also decreased. All the spectra of the copolymers are identical with that given in the literature for alternating MAN–St copolymers.<sup>18</sup> The different results ob-

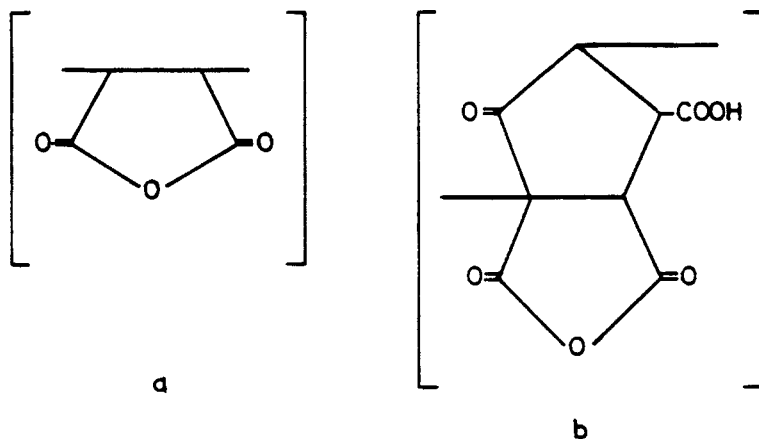


Fig. 6. MAN repeating units in unrearranged (a) and rearranged (b) forms.

TABLE IV  
Elemental Analyses of Sample 7 after the Amination

	Found	Calcd
C%	71.16	71.76
H%	8.11	7.67
N%	5.85	5.85
O%	14.88	14.72

tained from the elemental analyses and from the titrimetric methods may be explained with the rearrangement of the MAN units into the cyclopentanone structures. This was first suggested by Braun and co-workers in the homopolymerization of MAN with dibenzoyl peroxide as the initiator<sup>9</sup>(Fig. 6). Such a rearranged structure may lead to no changes in the results of the elemental analyses (by assuming that no decarboxylation takes place during the polymerization), but the free carboxyl group content of the copolymers after the hydrolyses will be far from the theoretical value.

Similarly, only the MAN units determined titrimetrically can react with *N*-diethylaminopropylamine to form the *N*-(diethylaminopropyl) maleamic acid units. For example, the elemental analyses of sample 7 after the amination corresponds to a copolymer with 30% *N*-(diethylaminopropyl) maleamic acid, 14% MAN, and 56% St and DVB units (Table IV).

## CONCLUSIONS

MAN-St-DVB copolymerization in the presence of dioxane-toluene (1:1) mixture as the diluent leads to the formation of porous copolymer beads. Compared to the St-DVB copolymers prepared in the presence of a non-solvating diluent such as cyclohexanol<sup>7</sup> more porous MAN-St-DVB copolymers are obtained at relatively low DVB concentration, i.e., at 1-3 mol % DVB. The porosity of the copolymers increases with decreasing MAN concentration in the feed due to the decrease in the copolymer yield. The results of the elemental analyses and the titrimetric methods suggest a possible rearrangement of the MAN units into the cyclopentanone structures.

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