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# Crosslinking polymerization of polyfunctional monomers by free radical mechanism

**Summary** — The crosslinked architectures based on diallyl maleate (DAM) obtained by suspension polymerization techniques have been studied. The influence of synthesis parameters on the structure of poly(diallyl maleate) [poly(DAM)] and copolymers of DAM with methyl methacrylate (MM) [poly(DAM-*co*-MM)] was also investigated. The effect of the diluents (*n*-butyl acetate or cyclohexanole) on the inner macroporous structure (apparent and skeletal density, pore volume, total porosity, cyclohexane uptake) has been studied. The experimental results showed that the values of the solvent uptake are strongly influenced by the diluent quantity as well as its solubility parameter.

**Key words**: crosslinking, radical polymerization, suspension polymerization, diallyl maleate, methyl methacrylate, copolymer, diluent, porosity.

## SIECIOWANIE WIELOFUNKCYJNYCH MONOMERÓW ZA POMOCĄ POLIMERYZACJI RODNIKOWEJ

**Streszczenie** — Przedmiotem badań był proces sieciowania na drodze polimeryzacji suspensyjnej maleinianu diallilu (DAM) i jego kopolimeru z metakrylanem metylu (MM). Określono wpływ warunków prowadzenia reakcji na strukturę otrzymanych poli(maleinianu diallilu) [poly(DAM)] i poli(maleinianu diallilu-*ko*-metakrylanu metylu) [poly(DAM-*co*-MM)]. Badano także wpływ rodzaju rozcieńczalnika (octan *n*-butylu lub cykloheksanol) i jego ilości na makroporowatą strukturę produktów. W tym celu wyznaczano gęstość pozorną, gęstość szkieletową, objętość porów, porowatość całkowitą i absorpcję cykloheksanu. Wyniki badań pokazują, że wielkość absorpcji rozpuszczalnika silnie zależy od ilości jak i parametru rozpuszczalności rozcieńczalnika.

**Słowa kluczowe**: sieciowanie, polimeryzacja rodnikowa, polimeryzacja suspensyjna, maleinian diallilu, metakrylan metylu, kopolimer, rozcieńczalnik, porowatość.

In recent years, there has been a significant progress in the design and synthesis of the crosslinked polymers due to their architectural and structural diversities and also potential applications as ion exchangers, adsorbents, gel permeation chromatography (GPC) column packing materials [1—8].

Generally, there are some conventional techniques in preparing crosslinked networks: solution, bulk, emulsion, dispersion or suspension polymerization [9, 10]. The sizes and the shapes of the obtained polymers are different because each method involves various mechanisms. Recently, the special features of the polymerization of allyl monomers referred as "allyl polymerization" have received great attention. Moreover, the number of publications on the topic of the polymerization of a series of allyl monomers such as, diallyl dicarboxylate, multiallyl hydroxycarboxylates, allyl oxalates, allyl vinyl monomers and others, as well as the mechanism of their polymerization [11] has also increased. Diallyl maleate (DAM) is a reactive polyfunctional monomer which can be homopolymerized [12] or used as a crosslinking comonomer with various monomers such as butyl acrylate [13], vinyl chloride [14] and styrene [15]. It has been observed that the crosslinking efficiency of diallyl maleate is higher than that of diallyl phthalate and ethylene glycol dimethyl acrylate [14].

In this work we present the synthesis by suspension polymerization techniques of several types of homopolymers based on DAM as well as copolymers based on DAM and MMA in order to elucidate the effect of synthesis parameters on the microstructural properties of copolymers. Copolymers formed with the incorporation of DAM have pendant allyl groups, making them suitable for various applications.

## EXPERIMENTAL

### Materials

Commercially available diallyl maleate (DAM, $C_{10}H_{12}O_4$), and methyl methacrylate (MM) were purchased from Fluka Chemical Company and distilled in vacum. The polymerization initiator, benzoyl peroxide, and the diluents *n*-butyl acetate (*n*-BA) or cyclohexanol

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(Cy) were delivered by Fluka Chemical Co. and were used as received.

The stabilizer, poly(vinyl alcohol) (PVA) and methanol used as solvent in the purification procedure of the obtained microparticles were purchased from Aldrich Chemical Co.

## Preparation of the microparticles

In order to study the influence of dilution of the polyfunctional monomer, two series of crosslinked polymers as beads using different ratio of diluents were prepared by suspension polymerization. The first series referees of crosslinked poly(DAM) prepared using Cy or *n*-BA as a diluent. The second series of referees of crosslinked copolymers based on DAM and MM [poly(DAM-*co*-MM)] were prepared under the same conditions.

The suspension polymerization process was carried out in a 1 dm$^3$ three-necked round-bottomed flask immersed in a thermostatic bath, fitted with a mechanical stirrer of variable rotation speed, a reflux condenser and a thermometer. The polymerization mixture which consisted of monomers (freed of inhibitors), variable quantities of diluents and initiator (1.5 % in relation to monomer weight) was poured into the flask containing aqueous solution of the stabilizer at temp. 60 °C.

The quantity of the diluents was expressed as a mass fraction ($w_g$) according to the following equation:

$$w_g = \frac{m_m}{m_m + m_s} \tag{1}$$

where: $m_m$ — *mass of monomers*, $m_s$ — *mass of diluents*.

The organic/aqueous phase volume ratio was 1/5. Polymerizations were performed at temp. 80 °C for 10 h and at 90 °C for 2 h.

Beads (diameter size 0.35—0.80 mm) of copolymers were washed with hot water, and extracted with methanol in a Soxhlet apparatus, and dried in a vacum oven at 50 °C for 48 h.

## Methods of characterization of the crosslinked structures

### FT-IR analysis

The FT-IR spectra of polymers were recorded with a Bruker Vertex 70 Spectrophotometer in the 5000—400 cm$^{-1}$ range with the KBr pellet technique.

### Optical microscopy

The optical microscope (Alpha STO5, Elektro-Optika Ltd.) was used to visualize the shape of beads. The dried beads were sprinkled on a glass plate, examined and images taken with a camera attached to the microscope.

### Characteristics of pore structure

The skeletal (ρ) and the apparent ($\rho_{ap}$) densities of beads were measured at temp. 20 °C by the picnometric methods with *n*-heptane and mercury, respectively [16]. The values of pore volume (*PV*), the so-called macroporosity were calculated using the following equation [17]:

$$PV = \frac{1}{\rho_{ap}} - \frac{1}{\rho} \tag{2}$$

where: $\rho_{ap}$ — *apparent density (g/cm$^3$)*, ρ — *skeletal density (g/cm$^3$)*.

The porosity (% *P*), which represents the percentage of the empty pores contained by the beads was calculated as follows:

$$\% \ P = \left(1 - \frac{\rho_{ap}}{\rho}\right) \cdot 100 \ \% \tag{3}$$

The solvent uptake coefficients of crosslinked polymers were determined at 500 rpm for 60 min by a method developed by Pepper [18]. The samples were put into a stainless steal cylinder referred to the bottom with a sieve and immersed in the solvent for 48 h after which they were centrifuged in order to determine solvent uptake.

## RESULTS AND DISCUSSION

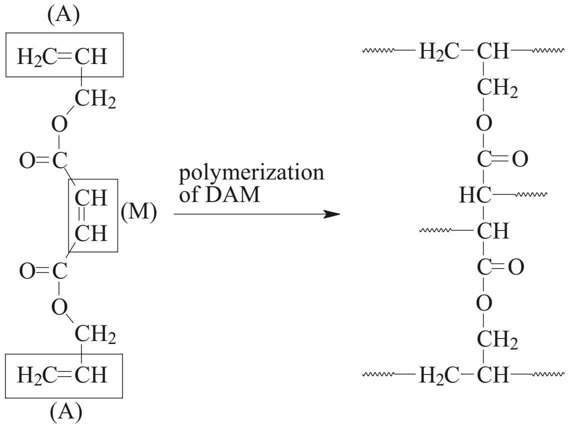
Four series of crosslinked beads were prepared by suspension polymerization technique under various synthesis conditions. The composition and geometry of the obtained products are presented in Table 1 and Figure 1, respectively.

The crosslinking polymerization of DAM may proceed according to reaction (eq. 4).

The structure of the crosslinked poly(DAM) can be elucidated taking into consideration of the special features of free-radical crosslinking copolymerization. The active end of the growing chains attaches itself to the monomers by propagation or reacts with other linear poly(DAM) by intermolecular crosslinking. The active end of the growing macroradical can attack the pendant

**Table 1. Compositions of crosslinked beads based on DAM**

| Sample code | Monomer content, % | | Diluent | |
|---|---|---|---|---|
| | DAM | MM | kind | $w_g$ |
| poly(DAM) | 100 | 0 | cyclohexanole | 0.8, 0.6, 0.5, 0.4, 0.35, 0.28 |
| poly(DAM) | 100 | 0 | *n*-butyl acetate | 0.8, 0.6, 0.5, 0.4, 0.35, 0.28 |
| poly(DAM-*co*-MM) | 68 | 32 | cyclohexanole | 0.8, 0.6, 0.5, 0.4, 0.35 |
| poly(DAM-*co*-MM) | 68 | 32 | *n*-butyl acetate | 0.8, 0.6, 0.5, 0.4, 0.35 |



(4)

where: *(A) — allylic bonds, (M) — maleic bond*

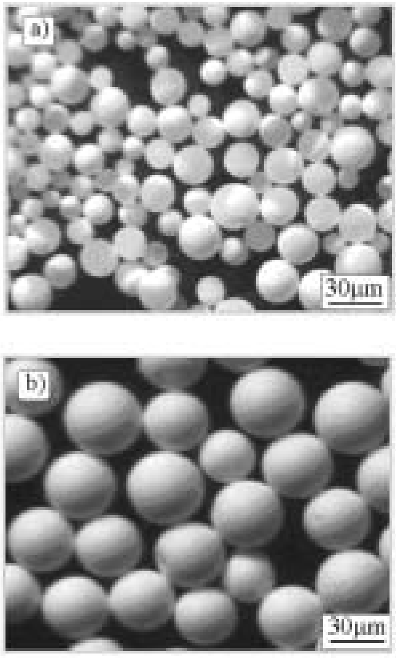
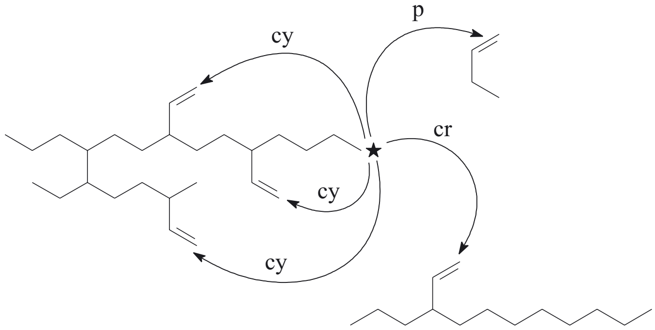
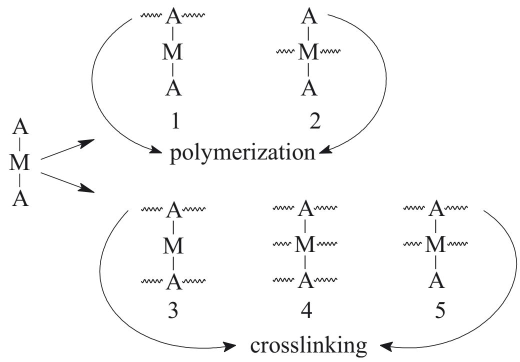


*Fig. 1. Optical micrograph of crosslinked beads obtained using n-butyl acetate with $w_g$ = 0.4: a) poly(DAM); b) poly(DAM-co-MM)*



*Scheme A. Possible reactions that can take place during the crosslinking polymerization of polyfunctional monomers: cy — cyclization, cr — crosslinking, p — propagation*



*Scheme B. The possible structures obtained by the copolymerization of DAM*

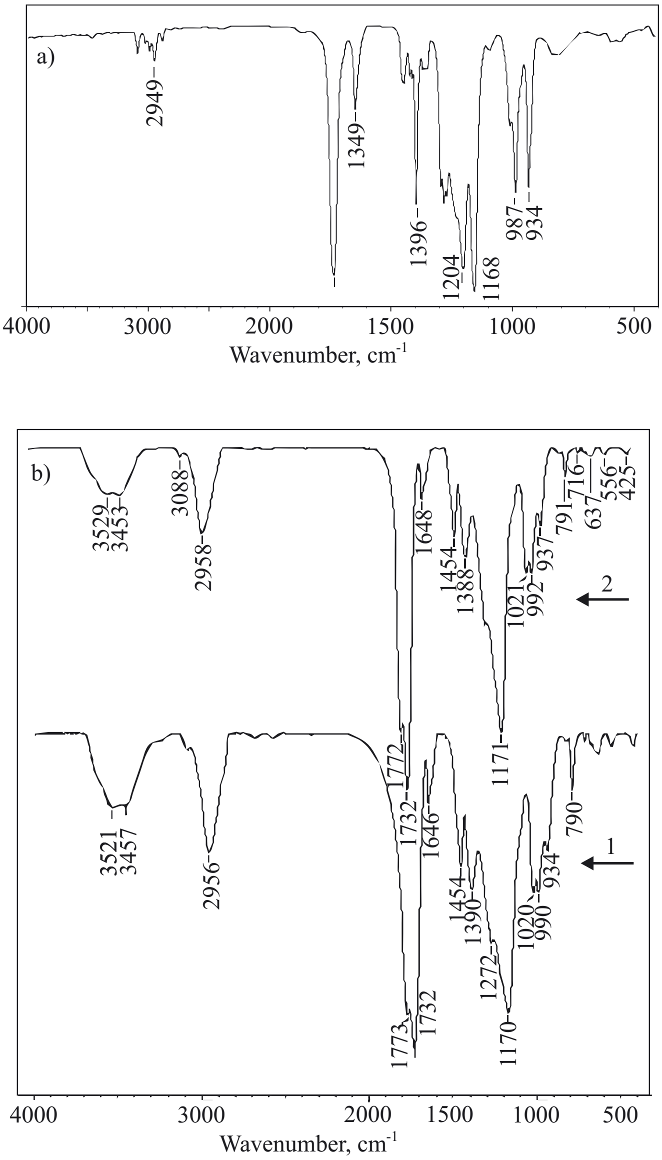


*Fig. 2. The FT-IR spectra for: a) DAM monomer, b) poly(DAM) prepared with n-butyl acetate as diluent and $w_g$ = 0.4 (1) and without diluent (2)*

double bonds on the same molecule by the intramolecular crosslinking, resulting in a linear chain containing small rings. The network performed by crosslinking polymerization also includes the cyclization, propagation and crosslinking reactions, as shown in Scheme A.

In the case of crosslinking polymerization of DAM there are two types of double bonds: allylic (A) and maleic (M). The kinetics of polymerization involves a large number of elementary reactions considered to be propagation reactions. The radical formed may have one of the structures presented in Scheme B.

Porous structures are formed in the presence of the diluent when the solvating power changes (the monomers become consumed and transformed into insoluble products and precipitate in the reaction medium). Taking into account the fact that the obtained compounds are insoluble, the investigation of their structures was done with specific methods of analysis.

Figure 2 shows representative FT-IR spectra of the monomer DAM (Fig. 2a) and poly(DAM) (Fig. 2b) prepared in the presence (spectrum 1) and absence (spectrum 2) of diluent. In every polymer spectrum, a decrease in intensity of the peaks at 1648 cm$^{-1}$, corresponding to the stretching vibration of vinyl groups indicating an incomplete double bonds conversion is observed.

The same phenomenon is observed in the case of adsorption bands at 987 and 934 cm$^{-1}$. A comparison between the spectrum of the polymer prepared with and without the diluent (Fig. 2b) reveals also, that there are no differences between both crosslinked polymers.

The changes in porous structure depend on the thermodynamic quality of the diluents, *i.e.* the values of the solubility parameter (δ). Some characteristics of the diluents and monomers used in synthesis are presented in Table 2.

**T a b l e 2. Some characteristics of diluents and monomers used**

| Substance | Characteristics | | | |
|---|---|---|---|---|
| | solubility parameter (MPa)$^{1/2}$ | density g/cm$^3$ | molar mass g/mol | molar volume cm$^3$/mol |
| *n*-BA | 17.31 | 0.86 | 116.16 | 135.06 |
| Cy | 22.40 | 0.93 | 100.16 | 107.69 |
| DAM | 18.82 | 1.073 | 196.21 | 183.36 |
| MM | 18.52 | 0.94 | 100.12 | 106.5 |

The solubility parameters of the poly(DAM) and poly(DAM-*co*-MM) were calculated from the structural formula using Small's — molar attraction constants [19] according to the equation:

$$\delta = d\Sigma Fi/M \qquad (4)$$

were: *Fi — the constant of the molar attraction of the atom or group contained by the structural unit of a polymer* [$(MPa)^{1/2} \cdot cm^3 \cdot mol^{-1}$], *d — density* [1.1759 g/cm$^3$ *for poly(DAM) and* 1.190 g/cm$^3$ *for poly(DAM-co-MM)*], *M — molar mass of the studied compound*.

The obtained values of $\delta_{poly(DAM)}$ = 20.95 (MPa)$^{1/2}$ and $\delta_{poly(DAM\text{-}co\text{-}MM)}$ = 18.75 (MPa)$^{1/2}$ were caused by the porous structure of studied polymers. The initial mixture is characterized by δ values, which were continuously modified due to the monomer polymerization. Also, the monomer/diluent ratio changes in a stepwise manner. Whenewer ($\delta_{polymer} - \delta_{solvent}$) is higher than $2 \cdot 10^3$ (MPa)$^{1/2}$, then the macroporosity influences only the small pore structure [20].

A small difference between the solubility parameters of diluent and monomer leads to stronger interaction between polymer chains and solvent during the polymerization process. The same observations were also recorded by authors in other researches, for crosslinked copolymers based on styrene-*co*-divinylbenzene and ethylene dimethacrylate esters [21, 22].

It is known that monomer dilution has a stronger influence on the apparent density for determination of pore sizes. An increase of the diluent quantity favours the processing of very spongy beads which posses a lower apparent density. The apparent densities of poly(DAM) and poly(DAM-*co*-MM) depend on the amount of diluents used as pore forming agent and important differences between the values of the apparent densities have been recorded for the two diluents. The apparent density of these polymers is plotted against the quantity of the diluents in Figure 3.

It should be noted that an increase in the Cy content in comparison to monomer content strongly influences the structure of poly(DAM-*co*-MM) (Fig. 3a). The variation of $w_g$ between 0.2—0.8 can lead to the crosslinked structures with larger variation of apparent density values (between 0.2—1.1 g/cm$^3$). In contrast, the cross-

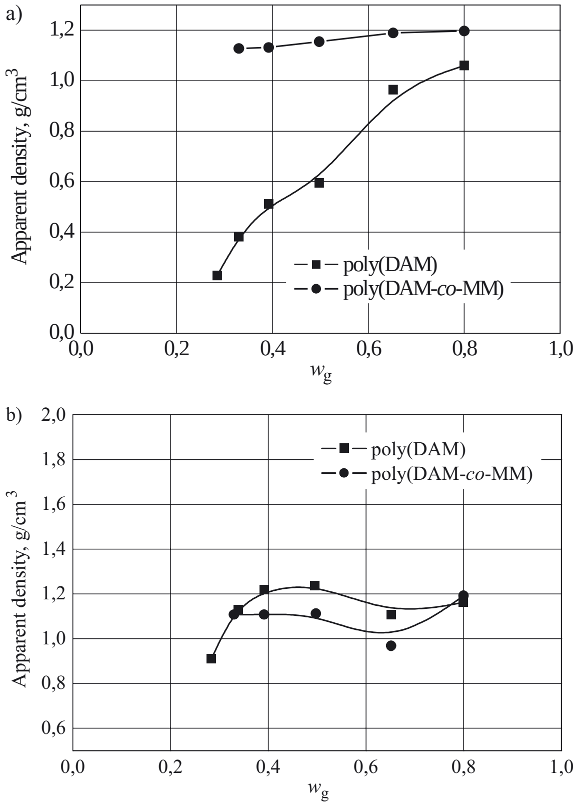


*Fig. 3. Values of apparent density as a function of mass ratio of monomer* ($w_g$) *for: a) cyclohexanole medium, b) n-butyl acetate medium*

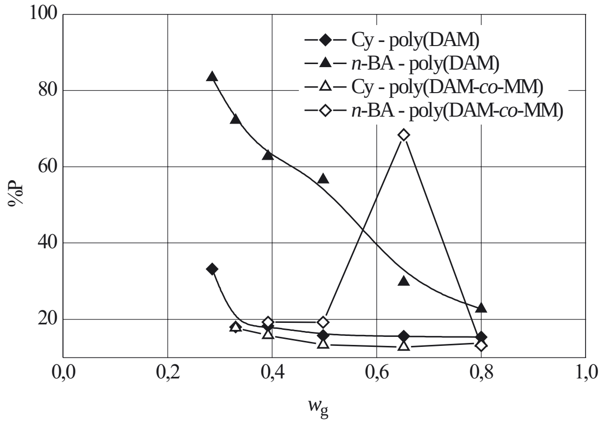


*Fig. 4. Values of the porosity of poly(DAM) and poly(DAM-co-MM) as a function of mass fraction of monomers ($w_g$)*

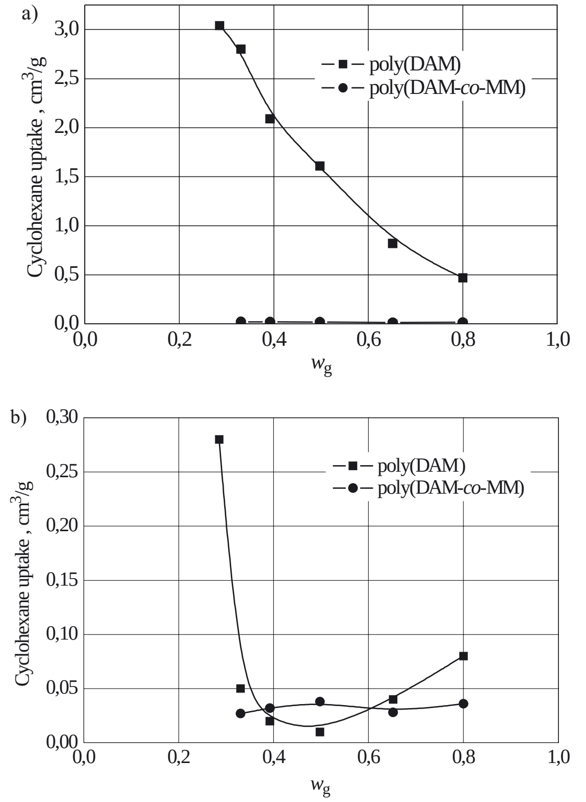


*Fig. 5. Cyclohexane uptake by the poly(DAM) and poly(DAM-co-MM) prepared with: a) cyclohexanole, b) n-butyl acetate*

linked polymers prepared in the presence of *n*-BA present low values of apparent density (Fig. 3b).

To illustrate the structural diferences of the studied beads the porous properties of crosslinked polymers as a function of the mass fraction of monomer are presented in Figure 4.

The crosslinked samples of poly(DAM) prepared with *n*-BA has the highest values of porosity. This is due to the low size of pores. These high values of porosity allow for good retention properties in solvents. Also, the retention coefficient of Cy is in good agreement with the porous structure of the copolymers as it was shown in Figure 5.

The samples of poly(DAM) obtained in Cy medium have an interesting feature of retention coefficient (Fig. 5a). Higher values of retention are assigned to samples prepared in presence of *n*-BA ($w_g$ = 0.28—0.35), while lower values of solvent uptake are observed in the case of poly(DAM-*co*-MM). As a general observation, we assume that the thermodynamics of the synthesis play an important role in the determination of the porous structure.

## CONCLUSIONS

The porous crosslinked beads were obtained through suspension copolymerization of DAM in the presence of Cy or *n*-BA. Depending on the thermodynamic conditions (diluent fraction and its solubility parameter), it is possible to obtain a large variety of porous crosslinked polymer structures based on DAM *i.e.* poly(DAM-*co*-MM) with tailored properties for specific applications in adsorbtion-retention processes.

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