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Preparation and properties of poly(methyl methacrylate) crosslinked with multimonomers

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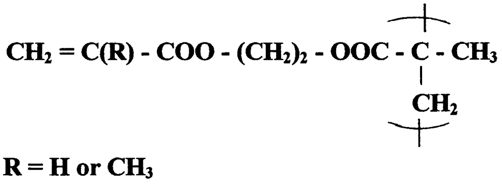
Summary

Multimonomers, such as poly(2-acryloyloxyethyl methacrylate) and poly(2-methacryloyloxyethyl methacrylate) were used as new macrocrosslinkers to crosslink poly(methyl methacrylate). The influence of the kind of macrocrosslinker, its molecular weight and amount on the crosslink density and some properties of the crosslinked polymers networks, such as swelling and mechanical properties (tensile strength and elongation at break) have been examined. The results obtained were compared with those for poly(methyl methacrylate) crosslinked with conventional crosslinker 1,4-butanediol dimethacrylate.

Introduction

Crosslinked polymer networks with the ability to absorb solvents have been widely used absorbents in medical, chemical and agricultural applications These materials are prepared mainly by radical polymerization or copolymerization of suitable monovinyl monomers in the presence of crosslinking agents such as divinylbenzene, diol dimethacrylates and diacrylates (1-8). Crosslinked polymers exhibit different properties depending on their crosslinking degree. In general, the crosslinking degree affects the swelling degree, pore size and mechanical strength of the network (7,9). Examining the crosslinking of methyl methacrylate with diol dimethacrylates possessing similar structure but different molecule length, Loshaek and Fox (6) have found that the efficiency of crosslinking clearly increases when the crosslinker concentration in the initial reaction mixture increases and when the molecule length of dimethacrylate decreases. Allen et al. (8) have found that with the increase in the crosslinker amount used to crosslink poly(2-hydroxyethyl methacrylate) the water absorption of the hydrogel decreases, while the hydrogel becomes harder and less elastic.

The present paper reports our findings concerning the efficiency of crosslinking poly(methyl methacrylate) (PMMA) with new macrocrosslinkers, such as poly(2-acryloyloxyethyl methacrylate) and poly(2-methacryloyloxyethyl methacrylate) (Scheme 1) comparing them with the crosslinking efficiency of a conventional crosslinker such as 1,4-butanediol dimethacrylate under the same conditions.



$$CH_2 = C(R) - COO - (CH_2)_2 - OOC - \overset{|}{\underset{\underset{|}{CH_2}}{C}} - CH_3$$

$R = H$ or CH_3

Scheme 1

Experimental

Materials

Methyl methacrylate (MMA) and 1,4-butanediol dimethacrylate (BDM) were freed from its inhibitor by shaking with 5 % aqueous KOH, washing with water, and drying over $CaCl_2$. They were then distilled under reduced pressure. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol. Dioxane was distilled over sodium.

Synthesis of multimonomers

Polydispersive multimonomers: poly(2-acryloyloxyethyl methacrylate) (MA) and poly(2-methacryloyloxyethyl methacrylate) (MM) were prepared by Schotten-Bauman's esterification of poly(2-hydroxyethyl methacrylate) (PHEMA) with acryloyl or methacryloyl chloride, according to the procedure described in our previous paper (10-11). MM was characterized by Mn = 26500 and Mw/Mn =2.2 whereas MA showed Mn = 28100 and Mw/Mw = 2.4. Three samples of poly(2-acryloyloxyethyl methacrylate) with Mn = 14700, Mn = 27200 and Mn = 49600, being characterized by a narrow molecular weight distribution (Mw/Mn = 1.32 - 1.38), were prepared by the esterification of PHEMA fraction with acryloyl chloride.

Synthesis of crosslinked PMMA

The free-radical polymerization of MMA in the presence of AIBN as initiator and variable amounts of the crosslinking agent was carried out for 24 h, gradually raising the process temperature from 45 to 70°C. Typical course of this process was as follows: 4.7 cm^3 of MMA, 0.02 g of AIBN, 1.6 cm^3 of dioxane and the selected crosslinking agent in amounts ranging from 0.35 to 3.0 mol% (calculated per single vinyl double bonds of crosslinker) in relation to the monomer were placed in polyethylene test-tubes which were then tightly closed and their content was thoroughly mixed. The polymerization was carried out in a laboratory drier under the following conditions: 2h at 45°C, 2 h at 55°C, 4 h at 60°C and 16 h at 70°C. The gradual temperature raising prevented blister formation in the crosslinked PMMA samples. Solid transparent products with cylindrical shapes were obtained. Disks with a diameter of about 12 mm and a thickness of about 2 mm were cut from them and used for investigating their swelling bahaviour.

In order to prepare samples for the mechanical testing of PMMA networks, the process was carried out by placing the same reaction mixture between glass plates (100 x 50 x 0.8 mm), previously siliconised with a dimethyldichlorosilane, and performing the polymerization under the same conditions. The resultant film was cut into 30 x 5 x 0.8 mm specimens to be tested for tensile strength and elongation at break.

Measurements

The swelling of crosslinked PMMA versus time was examined by determining the amount of absorbed swelling agent (toluene). About 0.3 g samples were dried at a temperature of 70°C under vacuum to a constant weight and then immersed in excess toluene at 25°C for various periods of time. The swollen samples were dried with a filter paper and weighed. The degree of swelling was calculated, using the following expression:

$$\text{Degree of swelling} = (W_t - W_o)/W_o$$

where W_t and W_o are weights of the disk at time t and zero (the dry state), respectively.

Crosslink density ν was determined from the equilibrium swelling data, employing Flory-Rehner's equation for a perfect network (12):

$$\nu = - \ [\nu_2 + \nu_2^2\chi + \ln(1-\nu_2)] / V_1(\nu_2^{1/3} - 0.5\nu_2)$$

where ν_2 is the volume fraction of polymer in the swollen network, χ is the Flory-Huggins interaction parameter between solvent and polymer (for the system PMMA-toluene, it was calculated from the data of the second virial coefficient to be 0.499) (13), V_1 is the molar volume of the solvent (106.3 cm^3/mol for toluene). The term ν is equal to ρ/Mc, where ρ is the density of the polymer and Mc the average molecular weight between crosslinks. The values of ν calculated by us refer, of course to real networks with inhomogeneous structures.

Mechanical properties of the examined samples was measured by means of a tensile testing machine of ZWICK (Germany), determining the tensile strength and elongation at break.

Results and Discussion

The crosslinked polymer forms very complicated network structures that is changing in the course of monomers conversion (14). Information about the network structure can be obtained from equlibrium swelling measurments. It is well known (15) that swelling depends on the crosslinking density and on the polymer—solvent intreaction parameter.

Figure 1 shows examples of curves illustrating the swelling of PMMA networks in toluene, obtained with various amounts (0.35 to 3.0 mol%) of polydispersive MA with Mn = 26500. As can be seen, the equilibrium swelling is reached after 48 h, its value decreases with increasing the macrocrosslinker concentration used in the initial reaction mixture.

A similar swelling course is shown by PMMA samples crosslinked with polydispersive MM with Mn = 28700, but their equilibrium swelling were somewhat higher. On the other hand, PMMA samples crosslinked with the same amounts of conventional crosslinker BDM show a considerably lower degree of swelling at equilibrium than that of PMMA crosslinked with macrocrosslinkers MA and MM. This seems to be associated with the higher crosslinking degree of PMMA when BDM with a lower molecular weight is used as crosslinker.

Moreover, they have, after swelling, considerably lower elasticity, transparency and initial shape retention than those of the samples crosslinked with macrocrosslinkers.

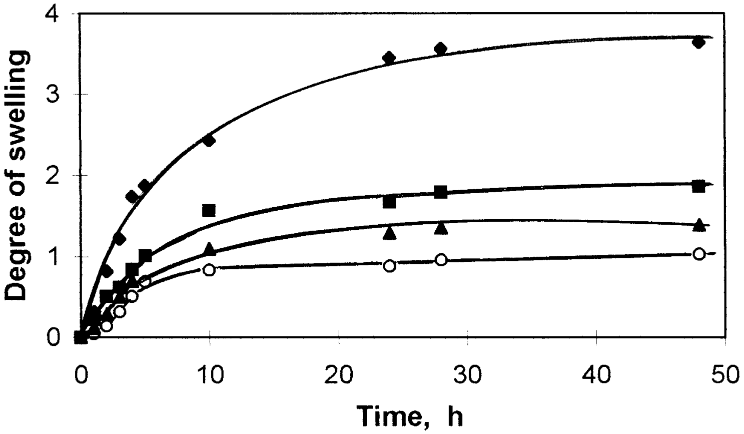


Figure 1. Swelling curves of PMMA crosslinked with various amounts of MA: (◆) 0.35 mol%; (■) 1.0 mol%; (▲) 1.6 mol%; (○) 3.0 mol%.

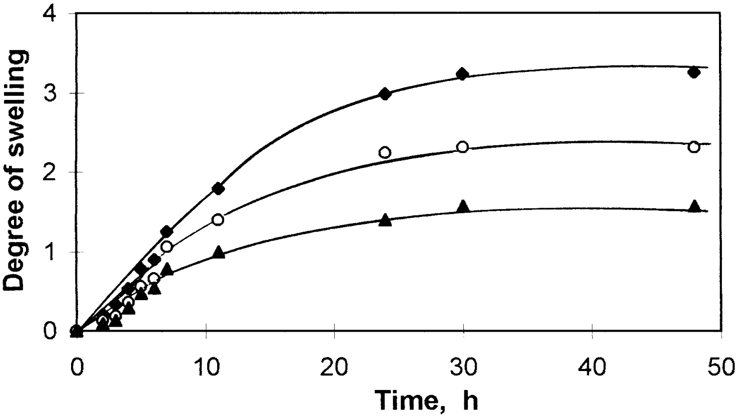


Figure 2. Swelling curves of PMMA crosslinked with MA with various molecular weights (♦) Mn = 49600; (o) Mn = 27200; (▲) Mn = 14700.

It is of interest to note the effect of molecular weight of macrocrosslinker (Mn = 49600, Mn = 27200 and Mn = 14700) with a low polydispersity index (Mw/Mn = 1.32 - 1.38) on the swelling of the PMMA networks, obtained with the same amount (1.0 mol%) of MA (Fig. 2). As can be seen, the obtained networks differ both in the swelling rate and the equilibrium swelling. The higher the molecular weight of the macrocrosslinker used for crosslinking, the higher is the equilibrium swelling degree of PMMA network. One may assume that with the increase in the molecular weight of the macrocrosslinker the obtained networks are less crosslinked.

The important structural parameters characterizing the crosslinked polymers are ν the crosslink density and Mc the average molecular weight between crosslinks. Their magnitude significantly affects the physical and mechanical properties of the crosslinked polymers.

Table 1 contains the results concerning the effect of the kind and amount of crosslinking agent on the characteristic parameters of the crosslinked PMMA. These data confirm that the values of ν and Mc are affected by the amount of the crosslinking agent used in the reaction mixture, while the kind of macrocrosslinker shows its effect only to an insignificant extent. The calculated values of crosslink density for PMMA crosslinked with macrocrosslinker are considerably lower than those for the conventional crosslinker BDM used in the same amount.

Based on the literature reports (16-21), one may assume that the networks resulted from the free-radical polymerization of MMA in the presence of BDM are inhomogeneous, namely they posses region having very different degrees of crosslinking density. Recent studies, however, indicate the existence of intramolecular crosslinking reactions in the form of cyclization and multiplate crosslinking which are responsible for these inhomogeneities (18,19). Though in our study, where the crosslinker concentration is low, cyclization is likely to be insignificant.

In the case of PMMA prepared with the use of polydispersive macrocrosslinkers such as MA or MM is likely to be more complex. Assuming that the macrocrosslinker is present in the reaction system in the from of a coil (the most probable shape of a flexible chain), one may believe that there will take place additional processes such as the intramolecular cyclopolymerization of double bonds of the crosslinker (22) as well as crosslinker between vinyl groups of various segments of the same macrosslinker. This may result in the increased inhomogeneity of the networks formed.

Table 1. Effect of the kind and amount of the crosslinking agent on the crosslinking parameters and the mechanical properties of PMMA networks

Cross-linker*	Amount of cross-linker % mol.	ρ g/cm^3	v_2	ν x 10^5 mol/cm^3	Mc g/mol	Elongation to break %	Tensile strength MPa
MA	0.35	1.176	0.1519	2.79	42180	18.0	28.6
MA	1.0	1.188	0.2813	17.37	6770	16.9	27.1
MA	1.6	1.190	0.3462	33.61	3522	12.8	30.2
MA	3.0	1.209	0.4379	73.82	1593	5.1	31.2
MM	0.35	1.179	0.1316	1.82	65500	17.8	26.8
MM	1.0	1.184	0.2779	16.70	7114	15.3	29.3
MM	1.6	1.193	0.3276	30.18	3960	-	-
MM	3.0	1.199	0.4178	62.88	1870	6.2	30.2
BDM	0.35	1.171	0.2928	19.70	5939	16.2	27.5
BDM	1.0	1.179	0.3630	39.80	2962	13.1	29.8
BDM	3.0	1.192	0. 4701	94.80	1257	5.9	34.5

*MA - poly(2-acryloyloxyethyl methacrylate) with Mn = 26500
MM - poli(2-methacryloyloxyethyl methacrylate) with Mn = 28700
BDM -1,4-butanediol dimethacrylate

Table 2. Effect of the molecular weight of poly(2-acryloyloxyethyl methacrylate) on the crosslinking parameters and mechanical properties of PMMA networks

Mn g/mol	Amount of cross-linker % mol.	ρ g/cm^3	v_2	ν x 10^5 mol/cm^3	Mc g/mol	Elongation to break %	Tensile strength MPa
49600	1.0	1.181	0.1883	5.11	23013	23.0	29.8
27200	1.0	1.189	0.2397	10.51	11312	19.3	27.9
14700	1.0	1.193	0.3148	24.80	4810	16.9	30.3

The results illustrating the effect of the molecular weight of MA (Mn = 49600, Mn 27200 and Mn = 14700) on the values of ν and Mc are given in Table 2. As can be seen, the increase in the molecular weight of macrocrosslinker is accompanied by the decrease in the crosslinking degree of PMMA network (ν decreases and Mc increases). The higher the macrocrosslinker molecular weight, the higher is its coiling degree in the reaction system. This will decrease the availability of the macrocrossliner double bonds in the free-radical polymerization with MMA and may cause Mc value to increase with the macrocrosslinker molecule lenght.

Some amount of unreacted double bonds in crosslinked vinyl polymers remains always hard to reach due to steric reasons (23). Based on IR measurments of PMMA samples (in KBr pellets, the characteristic absorption of vinyl double bonds at 1638 cm^{-1}) we found in them only an insignificant, unmeasurable content of unreacted vinyl groups. The structure of the networks will be the subject of further studies.

Table 1 includes also the results of examining the effect of the crosslink density on the mechanical properties of PMMA networks. The results obtained show that the increase in the crosslink density is accompanied by a clear decrease in their elongation at break and an insignificant increase in tensile strength. The kind of crosslinker is of no greater important. A similar tendency of changes in the elongation at break and tensile strength versus the crosslinker density is observed for PMMA crosslinked with macrocrosslinker MA having different molecular weight (Mn = 49600, Mn = 27200 and Mn = 14700), used in an amount of 1.0% (Table 2). The insignificant increase in tensile strenght for all the PMMA networks may be connected with their inhomogeneity.

Conclusion

Multimonomers can be used as effective macrocrosslinkes to form polymer networks from vinyl monomers. With the increase in the concentration of the examined crosslinking agents as well as with the decrease in the degree of polymerization of macrocrosslinker the produced PMMA networks show a lower equilibrium absorption of solvent. The PMMA crosslinked with macrocrosslinker are characterized by a lower solvent. The PMMA crosslinked with macrocrosslinker are characterized by a lower crosslink density than those of PMMA crosslinked with the same amount of conventional crosslinker dimethacrylate. The increase in the crosslinking degree of the PMMA networks brings about their decreased elongation at break in the case of all the examined crosslinkers, with their tensile strength being only slightly improved.

Acknowledgements

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