Polymer Bulletin 53, 277–284 (2005)
DOI 10.1007/s00289-005-0336-y

Polymer Bulletin

Synthesis and crosslinking properties of phenolphtalein dimethacrylate

Roman Jantas(✉), Halina Szocik, Dawid Stawski

Department of Physical Chemistry of Polymers, Technical University of Łódź, 90-924 Łódź, Poland
E-mail: rojan@p.lodz.pl

Received: 19 November 2004 / Revised version: 28 December 2004 / Accepted: 4 January 2005

Summary

By reacting esterification of phenolphtalein with methacrylate chloride, phenolphtalein dimethacrylate was obtained. Based on the results of elemental analysis, FTIR, ^{1}H-NMR and ^{13}C-NMR spectra, the structure of the product was proposed. The dimethacrylate was used as new crosslinker to crosslink poly(methyl methacrylate) (PMMA). The influence of the amount dimethacrylate on the crosslink density and some properties of the crosslinked polymers networks such as swelling, mechanical properties (tensile strength and elongation at break) and thermal stability were examined.

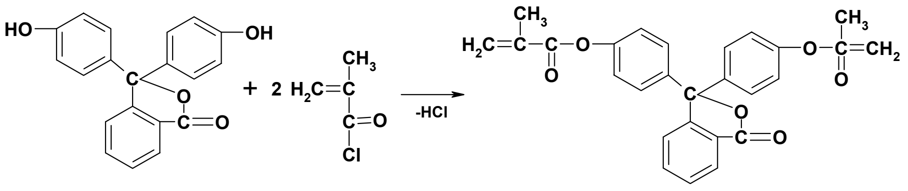
Introduction

Crosslinked polymers networks have been an interesting subject of research for many years due to their use in fields such as dentistry, microelectronics, or as absorbents in medicine and chemistry. These materials can be prepared by polymerization or copolymerization of appropriate vinyl monomers in the presence of low molecular weight crosslinking compounds such as divinylbenzene, diol di(meth)acrylates. or trimethylolpropane tri(meth)acrylate [1-8]. Crosslinked polymers exhibit different properties depending on their crosslinking degree. In general, the crosslinking degree affects the swelling degree, pore size, thermal stability and mechanical strength of the network [7,9]. Examining the crosslinking of methyl methacrylate with diol dimethacrylates possessing similar structure but different molecule lenght, Loshaek and Fox [6] have found that the efficiency of crosslinking increases with the increase in the lenght of dimethacrylate molecule and that the efficiency passes through a minimum with increasing dimethacrylate concentration in the reaction mixture. Numerous papers have presented mainly the results of studies of the crosslinking polymerization and copolymerization of vinyl monomers [10-13].

Less information was published on the physical properties of crosslinked networks. Dynamical-mechanical analysis [14,15] thermal stability [16,17] network densities [18,19] and surface hardness [19] are mostly selected for evaluating the properties of prepared networks.

The aim of the present study was to prepare phenolphtalein dimethacrylate be reacting phenolphtalein with methacryloyl chloride according to the following process

(Scheme 1) and to characterise the resultant product in respect of its physical and chemical behaviour, including also the assessment of the properties of polymeric networks obtained by the crosslinking polymerization of methyl methacrylate with the use of the prepared dimethacrylate.



Scheme 1.

Experimental

Materials

Methyl methacrylate (MMA) was freed from its inhibitor by shaking with 5 % aqueous KOH, washing with water, and drying over $CaCl_2$. It was then distilled under reduced pressure. Phenolphtalein (PP) a commercial product was used without further purification. Methacryloyl chloride (MCl) was prepared by reacting methacrylic acid with tionyl chloride [20]. Tetrahydrofuran (THF) was refluxed over CaH_2 and then distilled and kept over molecular sievers (4 Å). 2,2'- azobisisobutyronitrile (AIBN) was recrystallized from methanol.

Synthesis of phenolphtalein dimethacrylate (PDM)

PDM was prepared by Schotten-Baumann's interfacial esterification of PP with MCl. The optimum process parameters were found experimentally:

Solution A		
Solution of PP in THF	0.6 mol/dm^3 groups OH	1 vol.
Aqueous solution of KOH	3.0 mol/dm^3	1 vol.
THF		1 vol.
Solution B		
Methacryloyl chloride	1.2 mole-equiv. (to the hydroxyl groups in PP)	
THF		1.1 vol.
Toluene		0.2 vol.

Solution A was introduced into a three-necked flask equiped with a stirrer and a thermometer, cooled down to –8 °C, and then solution B was added dropwise. The reaction was carried out with intensive stirring for 60 min, and then the mixture was left for separation. The upper organic layer was separated from the lower one. Next, the organic layer was dried with anhydrous $MgSO_4$. Once the drying agent was filtered off, the solvent was evaporated and the raw product was crystallized in a methanol/water system. It was dried under reduced pressure at 30 °C. Yield 56%; m.p. = 47- 48 °C. ^{1}H-NMR ($CDCl_3$): δ = 2.05 (s,3H,α-CH_3), 5.76 and 6.34 (t,2H,CH_2=), 7.05 ÷ 8.07 (m,12H,ArH). ^{13}C-NMR ($CDCl_3$): δ = 18.38 (-CH_3), 123.98, 129.10 (C=CH_2), 121.58, 125.95, 127.46, 128.21, 129.46, 133.64, 134.26, 137.92, 150.95

(CAr), 165.38, 169.27 (C=O). FTIR (cm^{-1}): 1736, 1772 (C=O); 1637 (C=C). Anal. Calcd. for $C_{28}H_{22}O_6$ (454.48): C, 74.00%; H, 4.88%, Found: C, 73.42 %; H, 4.79%

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 40 to 75 °C. Typical course of this process was as follows: 4.4 cm^3 of MMA, 0.02 g AIBN and the crosslinking agent in amounts ranging from 0.5 to 5.0 mol% (calculated per single double bound of crosslinker) in relation to the monomer were placed by means of a syringe between two glass plates seperated by a silicon spacer (120 x 50 x 0.9 mm). The glass plates were siliconised with a dimethyldichorosilane. The polymerization was carried out in a laboratory drier under the following conditions: 2 h at 40 °C, 4 h at 55 °C and 18 h at 75°C. The gradual temperature raising prevented blister formation in the crosslinked PMMA samples. After removal of the glass plates, the films obtained were dried at 75 °C. Two kinds of samples were cut out from the films: with the dimensions 15 x 10 x 0,9 mm for investigating their swelling behaviour and with the dimensions 40 x 5 x 0.9 mm for mechanical testing (tensile strength and elongation).

Before the examination of the samples were immersed in a large excess of toluene for about 48 h at 25 °C remove the non-crosslinked material and then were dried at room temperature for about 24 h, and further dried in a 75 °C under vacuum to a constant weight.

Measurments

Infrared spectra were recorded using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) instrument. ^1H-NMR and ^{13}C-NMR spectra were obtained using a Bruker DPX 250 MHz spectrometer with $CDCl_3$ as solvent and TMS as an internal reference.

The thermogravimetric (TG) investigations were performed using a TGA-7 thermobalance of Perkin-Elmer in a nitrogen atmosphere (sample of about 5 mg, a heating rate of 15 °C min^{-1} within the temperature range from 50 to 550 °C).

The swelling of crosslinked PMMA versus time was examined by determining the amount of absorbed swelling agent (toluene). About 0.18 g samples were immersed in excess THF 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:

$$\text{Degree of swelling} = [(W_t - W_o)/W_o] \times 100 \qquad \textbf{(1)}$$

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

The number average molecular weight between crosslinks M_c was determined from the equlibrium swelling data, employing Flory-Rehner's equation for a perfect network [21].

$$\overline{M}_c = V_1 \rho_p \frac{\left(\phi_p^{1/3} - \phi_p / 2\right)}{\left[\ln\left(1-\phi_p\right) + \phi_p + \chi\phi_p^2\right]} \qquad \textbf{(2)}$$

where: M_c is the number average molecular weight between crosslinks, ϕ_p is the volume fraction of polymer in the swollen network, χ is the Flory-Huggins interaction parameter between solvent and polymer, (for PMMA - toluene it was calculated from the data of the second virial coefficient to be 0.499) [22]. V_1 is the molar volume of the solvent (106.3 cm^3/mol for toluene), ρ_p is the density of the polymer. The values of M_c calculated by us refer, of course to real networks with inhomogeneous structure. 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. The samples dimensions were 40 x 5 x 0.9 mm and the samples length between the clamps was 10 mm. All the values given are means of six measurements.

Results and discussion

Spectral characterization of PDM

The hydroxyl groups of the PP were esterified by introducing of methacrylate crosslinkable groups. The chemical structure of PDM was determined by means of FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy as well as elemental analysis.

Figure 1 shows of FTIR spectra of PDM (Fig. 1a) as well as of the initial PP (Fig.1b). PDM exihibit an absorption band additional, to the initial PP, at 1637 cm^{-1} (>C=C<), and 1772 cm^{-1} (>C=O) in ester groups. On the other hand, there disappears the band in the range 3630—3050 cm^{-1} derived from the hydroxyl groups of PP.

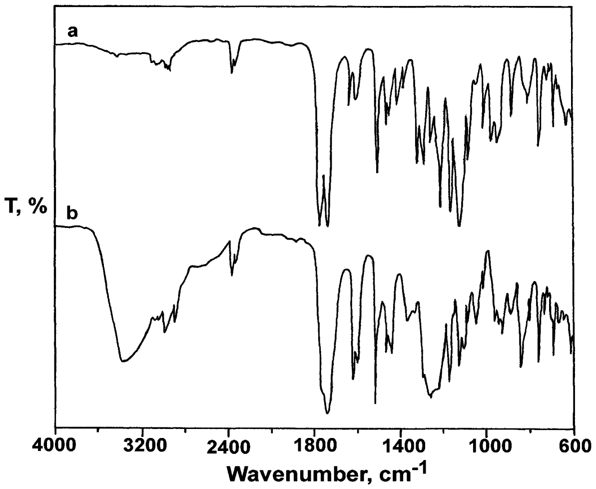


Figure 1. IR spectra of: (a) PDM; (b) PP

The ^{1}H-NMR spectrum of PDM (Figure 2) shows the following chemical shifts of protons: for α-CH_3 at 2.06 ppm, for CH_2=C< at 5.82 ppm and 6.46 ppm, for ArH at 7.13 - 8.08 ppm.

Similar to ^{1}H-NMR, the structure of PDM was confirmed by ^{13}C-NMR spectrum (no shown) where different types of resonance peaks were observed for various carbon

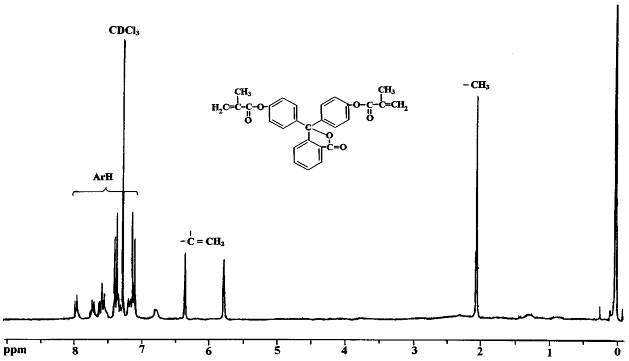


Figure 2. ^{1}H-NMR spectrum of PDM

atoms. For instance, two well-separated resonance peaks were obtained for carbon atoms of two carbonyl groups of at 165.38 and 169.27 ppm as well as resonance peaks for double bond carbons at 123.98 and 129.10 ppm.

The analysis FTIR, ^{1}H-NMR and ^{13}C-NMR spectra and the results of elemental analysis confirms the chemical structure of the obtained of PDM.

The samples of PMMA crosslinked with PDM are rigid, transparent and insoluble in solvents for the homopolymer of methyl methacrylate.

The crosslinked polymer forms very complicated structures of a network that is changing in the course of conversion of the monomers [23]. Information about the network structure can be obtained from equilibrium swelling measurements. It is well known [21] that swelling depends on the crosslinking density and on the polymer-solvent interaction parameter.

Figure 3 shows of curves illustrating the swelling of PMMA networks in toluene, obtained with various amounts (0.5 to 5 mol%) of PDM. As can be seen, the equilibrium swelling is reached after about 60 h, its value decreases with increasing the dimethacylate concentration used in the initial reaction mixture.

The fraction of materials extractable with toluene, a good solvent for PMMA was in all cases lower than 2% of wt.

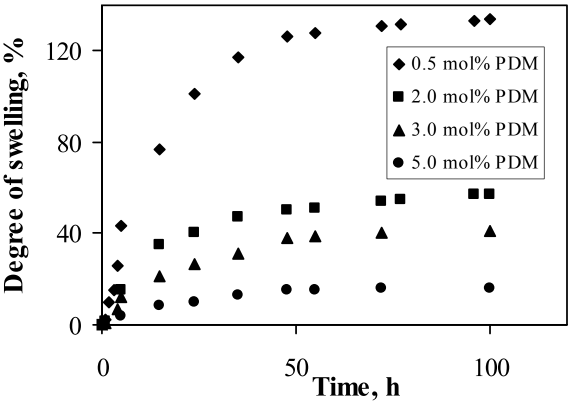


Figure 3. Swelling curves of PMMA crosslinked with various amounts of PDM

The important structural parameter characterizing the crosslinked polymers is M_c the number average molecular weight between crosslinks, which is directly related to the crosslink density. The magnitude of M_c of significantly affects the physical and mechanical properties of the crosslinked polymers.

In Table 1 are given the results that show the effect of the crosslinker on the crosslinking density, M_c of PMMA. As follows from these data, the value of M_c depends on the quantity of the crosslinker used in the reaction mixture, the higher the crosslinker content, the denser is the crosslinking of PMMA.

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

Sample	Amount of cross-linker, % mol	ρ g/cm^3	V_1	M_c g/mol	Elongation to breake %	Tensile strength MPa
PMMA1	0.5	1.171	0.3614	2953	23.3	29.9
PMMA2	2.0	1.178	0,5627	645	21.9	38.2
PMMA3	3.0	1.187	0.6439	376	21.0	42.6
PMMA4	5.0	1.196	0.8213	217	19.6	45.2

Table 1 shows also the results that reveal the effect of crosslinker on the mechanical strength of PMMA networks. With the increase in the crosslinker concentration (0.5 – 5.0%mol), the density of PMMA crosslinking also increases, which results in an increased tensile strength and slightly decreased elongation at break.

It is generally known that considerable influence on the thermostability of polymers is exerted by their chemical structure – the strength of bonds between atoms of macromolecules. The thermal stability of polymers depends also to a great extent on the character of the macromolecular structure (linear, branched or crosslinked). As a rule, branched polymers are less thermally resistant than linear polymers, while crosslinking increases thermostability.

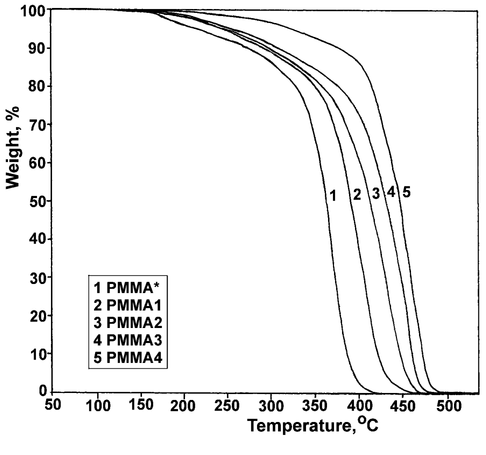


Figure 4. TG curves of PMMA networks and untreated PMMA in inert atmosphere

Table 2. Thermal stability indices of PMMA networks

Sample	Thermal stability indices	
	T_5	T_{50}
PMMA1	240	380
PMMA2	244	415
PMMA3	255	435
PMMA4	325	450
PMMA*	189	370

T_5, T_{50} – temperature of 5 and 50% mass loss of the sample
PMMA*- untreated M_n = 213000 g/mol

Fig. 4 shows the thermograms of untreated PMMA (curve 1) and PMMA samples crosslinked with various quantities of PDM (curves 2 – 5). Table 2 includes the values of temperatures at which PMMA samples lose their weight from 5% to 50% as determined from the TG curves. Both the TG curves and thermal stability indices show that the crosslinked PMMA samples have a higher thermal stability than that of untreated PMMA, which increases with the density of crosslinking. This is probably connected with the fact that the lower the number-average molecular weight of the chains between the network nodes, the more difficult is the exceeding of the limiting oscillation amplitude that leads to bond cleavage.

Conclusions

The studies performed have shown that the esterification of PP with methacrylate chloride by Schotten-Baumann′s method results a new phenolphtalein dimethacrylate. Dimetacrylate can be used as effective crosslinkers to form polymer networks from vinyl monomers. With the increase in the PDM content in the initial reaction mixture, the formed PMMA networks show a lower solvent absorption under equilibrium and a higher crosslinking density. With increasing PMMA crosslinking density, the elongation at break of PMMA slightly decreases and its tensile strength increases. Based on the TG analysis results, one can conclude that the increase in the PMMA crosslinking density is accompanied by the increase in its thermal stability.

References

1. Dusek, K (1982) Developments in Polymerization, Vol, RN Howard, Ed., Applied Science, London, p. 143.
2. Okaya O, Naghash HJ, Capaek I (1995) Polymer 36: 2413
3. Naghhash HJ, Okaya O, Yildirim H (1995) Polymer 36: 477
4. Davis TP, Huglin MB (1991) Angew Makromol Chem 189: 195
5. Arriola DJ, Cutie SS, Henton DE, Smith P (1997) J Appl Polym Sci 63: 491
6. Loshaek S, Fox TG (1953) J Am Chem Soc 75: 3544
7. Akelah A, Moent A (1990) Functionalized Polymers and Their Applications, Ed, Champan and Hall, London
8. Allen PEM, Bennet DJ, Williams DRG (1992) Eur Polym J 28: 347
9. Weber M, Stadler R, (1988) Polymer 29: 1097
10. Naghash HJ, Okay O, Yildirim H (1995) J Appl Polym Sci 56: 477
11. Hamielec AE, Tobita H (1992) Ullmann's Encyclopedia of Industrial Chemistry, VCH Publishers, Weihheim, Germany, p. 305

12. Okay O, Naghash HJ, Capek J (1995) Polymer 36: 2413
13. Okay O (1988) Makromol Chem 189: 2201
14. Nabeth B, Gerard JF, Pasculat JP (1996) J Appl Polym Sci 30: 2113
15. Anseth KS, Bowman CN, Peppas NA (1993) Polym Bull. 31: 229
16. Kurdikar DL, Peppas NA (1994) Polymer 35: 1004
17. Cook WD (1992) Polymer 33: 600
18. Duŝek K (1993) Collect Czech Chem Commun 58: 1109
19. Macucelli G, Gozzelino G, Bongiovanni R, Priola A (1996) Polymer 37: 2565
20. Arbuzowa IA, Medvedeva L, Plotkina SA (1956) Zh Obshch Khim 26: 1127
21. Flory PJ (1953) Principles of Polymer Chemistry, Cornell University Press Ithaca NY 1953
22. Brandrup J, Immergute EH (1974) Polymer Handbook 2nd Ed, Wiley, New York
23. Duŝek K (1993) Collect Czech Chem Commun 58: 2245