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Preparation, Characterisation and Crosslinking Properties of Water-soluble Multimonomers

Abstract
Multi-functional water-soluble cross-linking polymeric quaternary ammonium salts with allyl groups have been synthesised. These compounds were then used to prepare hydrogels of poly(acrylic acid) by cross-linking in a swollen state. The samples obtained were tested for compression and tensile strength, and Young's modulus was determined within the range of low elastic strain. The hypothesis that it is possible to synthesise hydrogel networks with multiple nodes is put forward.

Key words: *multimonomers, cross-linking, poli(acrylic acid), properties.*

Introduction

Commonly used cross-linking compounds such as divinylbenzene, ethylene diacrylate or trimethylolpropane triacrylate etc. mostly contain two or three vinyl groups [1,2]. The use of such cross-linking compounds results in the formation of polymeric networks with a cross-linking point distribution similar to random distribution. It was mentioned in our papers [3,4] that it was possible to use multimonomers as cross-linking compounds which should provide a specific, non-statistic distribution of cross-linking points. The properties of such polymeric networks were studied to only a limited extent.

Recently, more and more interest has been aroused in hydrogels obtained not by polymer cross-linking followed by its swelling, but by cross-linking in a swollen state [5]. Thus, water solubility of a cross-linking compound is a prerequisite for hydrogel formation. It should be emphasised that the hydrogels described in this paper might, after further investigation, be applied in composites with textile materials.

The aim of the present study was to prepare cross-linking compounds such as water-soluble multimonomers to be used for polymeric network formation and to test selected properties of the hydrogels obtained. These hydrogels can be applied in composites of textile materials.

Allyl derivatives of polymers containing the tertiary amine groups poly(N-allyl-N,N-dimethylmethacrylo-ethyl ammonium bromide) (PDAMBr) and poly[4-(N-allylpyridine) ethylene bromide] (PVPBr) were selected as cross-linking compounds.

In addition, it was of interest to use cross-linking compounds which are capable of creating covalent bonds and interacting with the monomer under polymerisation through groups with electric charges. As is known, such systems are used in matrix polymerisation, which sometimes results in a ladder-type structure.

Experimental Data

Materials

- Poly(N,N`-dimethyloaminoethyl methacrylate) (PDAMA) was obtained by radical polymerisation of the monomer in toluene initiated by AIBN. M_n - measured by the osmometry method was 167,000.
- Poly(4-vinyl pyridine) (P4VP) (Polyscience M_w= 50,000) was used without purification.
- Acrylic acid (Fluka) was distilled under reduced pressure. Ammonium persulphate - analytical grade from P.O.Ch. (Polish Chemical Reagents).

Synthesis of multimonomers

A typical synthesis of PDAMBr was as follows: 0.5 g (3.2 mmole) of PDAMA in 10 cm^3 of ethanol was mixed with 2 cm^3 (19 mmole) of allyl bromide and left at room temperature for 24 h. Then, the excess allyl bromide was distilled off under vacuum and the product was precipitated with n-heptane. Next, the product was redissolved in ethanol, precipitated with n-heptane and dried under vacuum at room temperature. The brittle product is soluble in water and ethanol, and insoluble in n-heptane and chloroform. The synthesis of PVPBr was carried out by the same method as that described above.

Synthesis of cross-linked poly(acrylic acid)
To select suitable conditions for cross-linking, a series of experiments was performed according to the following procedure: a different amount (0.05-0.2 g) of PDAMBr or PVPBr was dissolved in 1 cm^3 of a solution containing 1 g ammonium persulphate in 50 cm^3 of water. Then, 1 g of acrylic acid and 1 cm^3 of water was added. The samples were heated at 48 °C for 20 min; next, the temperature was lowered at a rate of 10°C/h, and the sample was left at room temperature for 24 h.

The samples were taken out and immersed in an excess of water to reach equilibrium swelling. The degree of equilibrium swelling was calculated from the equation:

Table 1. The conditions of samples synthesis and swelling properties.

Series no.	Acrylic acid	Type of crosslinker	Concentration of crosslinker	Persulphate solution	Degree of swelling	k	Percent of sol fraction
	cm^3	-	g/dm^3	cm^3	g/g	-	%
1	1	PDAMBr	6.67	1	80.50	98	-
2	1	PDAMBr	16.67	1	16.49	90	21.2
3	1	PDAMBr	23.33	1	-	-	-
4	1	PVPBr	33.33	1	-	-	-
5	1	PDAMBr	33.33	1	4.00	77	22.3
6	1	PDAMBr	66.67	1	2.39	112	22.8

$$z = (m_t - m_0)/m_0 \quad (1)$$

where:
m_t - sample weight after swelling,
m_o - dry sample weight.

Moreover, it was found that the cross-linking of the system already started at room temperature after 24 h, but the hydrogels obtained possess weak mechanical properties. A series of samples (listed in Table 1) with various shapes containing various quantities of the cross-linking compound were prepared in order to test their mechanical properties.

Measurements

^{1}H NMR spectra were obtained using a Brucker DPX 250 MHz spectrometer with $CDCl_3$ as a solvent and TMS as an internal reference. The samples were prepared in various shapes such as rods with a diameter of about 10 mm; monofilaments with a diameter of 2-3 mm carried out the process in teflon or polyethylene tubes with the appropriate diameter.

Testing the mechanical properties of the hydrogels obtained after equilibrium swelling

Compression tests were carried out using a Höppler-Konsistometer (Medingen/ Dresden). Prior to testing, the rod-shaped samples were swollen in water for several days in order that the tests could be performed for samples under equilibrium swelling. Measurements were carried out within a recovery range, i.e. for low strains. Tensile strength was tested by means of a Zwick 1120 tensile testing machine from Zwick Materialprüfung at an initial load of 10 cN, and a rate of 100 mm/min for a specimen with an initial length of 10 mm. The monofilament samples with a diameter of 2-3 mm were swollen to equilibrium prior to testing. The calculated values of Young's modulus for the samples under investigation are listed in Table 2. A series of tests of elongation versus load was also performed, by applying a static load and measuring the elongation by means of a micro-cathetometer. Samples with a diameter of 2-5 mm were 4-5 cm long; however, the precision of this method was lower than that described earlier.

Results and Discussion

The ^{1}H NMR spectrum of PDAMBr in D_2O (Figure 1) shows well separated proton bands of the allyl group (one proton at 6.11 ppm, two protons at 5.82-5.75 ppm), peaks of CH_3 at the nitrogen atom (3.20 ppm), as well as slightly separated bands of CH_2 group. From the ratio of the proton peaks of the allyl group to the remainder, it follows that the product contains practically 100% quaternary amonium groups. The ^{1}H NMR spectrum of obtained PVPBr, as shown in Figure 2, also confirms the structure.

As an example, for the sample of series 2 the stress-strain relationship for compression and elongation of the sample is

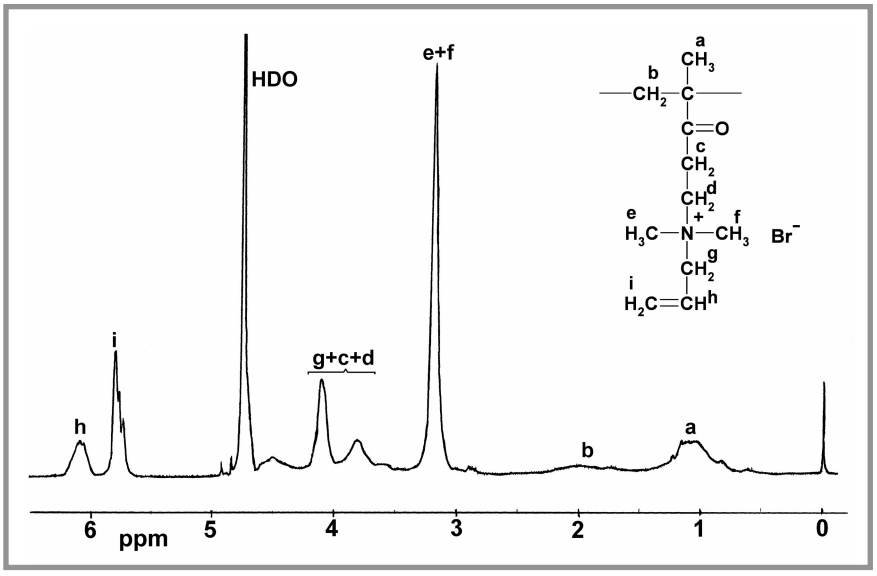

Figure 1. ^{1}H-NMR spectrum of PDAMBr.

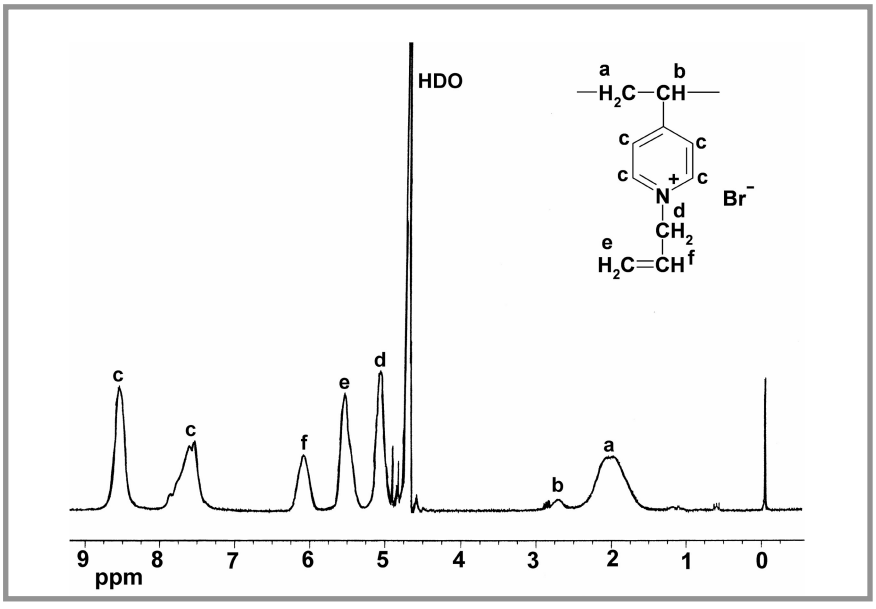

Figure 2. ^{1}H-NMR spectrum of PVPBr.

shown in Figure 3(A and B). 10 measurements were performed for each series, the average values of Young's modulus were calculated and the results are given in Table 2.

The samples of acrylic acid hydrogel crosslinked by PVPBr were similarly synthesized and tested. The samples obtained showed some macroscopic heterogeneity. However, the Young's modulus calculated was close to that obtained for the cross-linking compound from PDAMBr. One example (series 4) is shown in Table 2.

The relation between the swelling ratio and network structure for the swelling of ionic networks was given by Flory [7] for networks with a statistical distribution of nodes.

Accepting the simplifications published in [6] (stable interaction parameter polymer-solvent, and the same efficiency of the crosslinker), the degree of equilibrium swelling z should be proportional to the crosslinker concentration to the power of -0.6 [6]:

$$z = k \cdot c^{-0.6} \quad (2)$$

This means that for the product $k = z$, $c^{0.6}$ should be constant. As we can see from Table 1, the calculated value k is scattering but is approximately constant. This may be connected with the statistical distribution of multiple nodes in the networks under investigation.

The very high absorption of networks obtained with low concentration of crosslinkers can be applied in preparing superabsorbent non-weaving composites, which will be the subject of our further investigations.

Conclusions

The water-soluble cross-linking compounds prepared react specifically when the monomer used to form networks has acid groups. The cross-linking compound obtained by quaternising poly(N,N'-dimethylaminoethyl methacrylate) with allyl bromide contains groups capable of creating covalent bonds, while the charges generated in the cross-linking compound are capable of interacting with acid monomer molecules. In addition, the cross-linking mechanism can be affected by the presence of ammonium groups, which are known to have catalytic effects on the decomposition of peroxide initiators. It is possible that during the cross-linking process a template process partially occurs, consisting in initial orientation of monomer molecules followed by the formation of a local ladder structure. Thus, the created network is likely to possess 'multiple nodes'. However, additional studies are required to confirm this structure.

The hydrogels prepared have the consistency of soft rubber. Cross-linking with the use of the synthesised compound proceeds very easily even under mild conditions, which suggests that it is possible to use these hydrogels as, for instance, carriers of less stable biocides. The very high absorption of networks obtained with a low concentration of crosslinkers can be applied in preparing superabsorbent non-weaving composites, which will be the subject of our subsequent investigations.

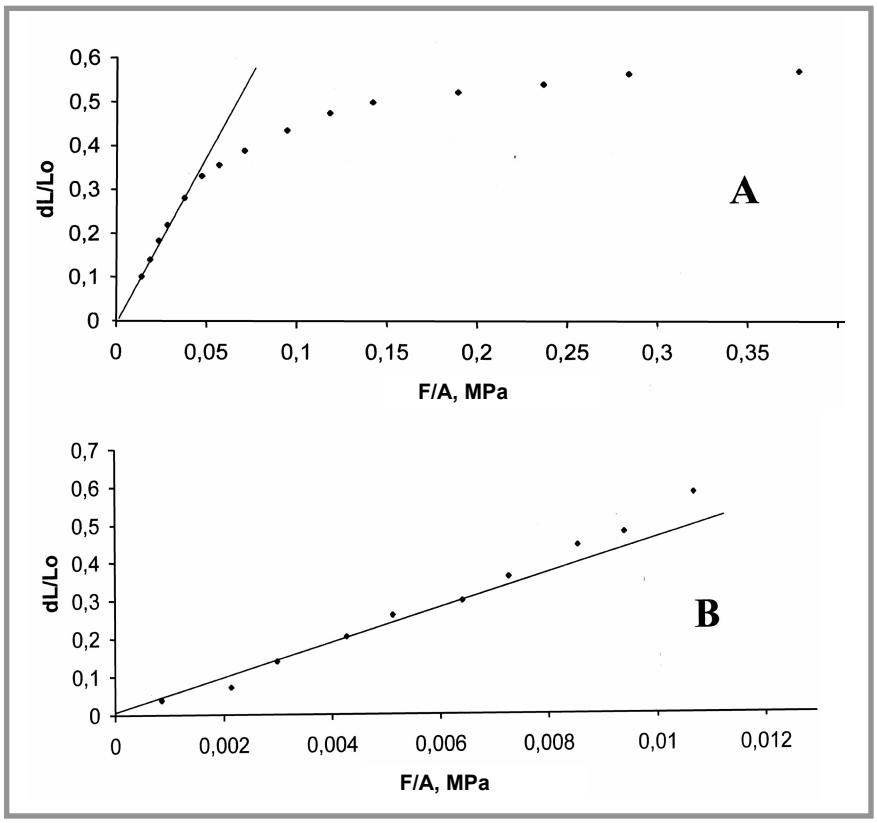

Figure 3. *Strain ΔL/Lo as a function of stress for a sample from series 2 (see Table 1): A - compression; B - elongation.*

Table 2. *Average values of Young's modulus.*

No of series (see Tab. 1)	Young`s modulus compression, MPa	Young`s modulus elongation (static), MPa	Young`s modulus elongation (testing machine), MPa
2	0.142	0.023	0.028
3	0.201	-	0.044
4	-	0.075	-
5	0.257	0.095	0.053
6	0.398	0.106	0.077

Acknowledgements

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