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Structural properties of poly(ether) macromonomer based hydrogels

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Summary

The major part of the present work discusses the synthesis and the properties of a series of hydrogels obtained by free radical copolymerization of α,ω–methacryloyloxy poly(ethylene oxide) (PEO) or poly(1,3-dioxolane) (PDXL) macromonomers. The influence of several parameters such as macromonomer molar mass, comonomer concentration, type of solvent, and crosslinking concentration on the weight degree of equilibrium swelling, the uniaxial compression modulus and the thermodynamic interaction parameter was investigated systematically. Hydrogels whose elastic chains are constituted of a short central PDXL block surrounded by two hydrophilic PEO blocks were prepared according to the same strategy. PDXL is known to be sensitive to acidic degradation due to the presence of acetal groups. Therefore, once placed in acidic media (in water or in an organic solvent) network degradation occurred. The solid-state properties of the different PEO or PDXL co-networks were examined by DSC, and compared to those of linear PEO or PDXL chains and to those of homopolymeric PEO or PDXL networks.

Introduction

Increasing interest has been devoted in past sixty years to polymer networks. The properties and structures of crosslinked polymers have been shown to depend closely on the process by which they are formed. Crosslinking methods can be classified in three groups: the first approach to design networks results from the creation of bridges between pre-existing linear chains by vulcanization, peroxydation or irradiation. The second involves crosslinking polycondensation or free-radical crosslinking copolymerization. The third method, the most recent one, is based on the reaction of well-defined bifunctional precursors with multifunctional low molar mass compounds exhibiting antagonist functions. The latter method yields the so-called model-networks, characterized by elastic chains of controlled length and, in most cases, of

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controlled functionality. Therefore such networks have been extensively used to test the validity of thermodynamic and rubber elastic theories, by establishing a relation between the structural parameters of the networks (such as molar mass of the elastic chains or preparation conditions) and their specific properties [1].

In recent years, the synthesis of networks by free radical polymerization of bifunctional macromonomers has given rise to increasing interest since this approach is easy to perform, applicable directly in water, and nevertheless yields hydrogels of controlled structural parameters [2-4]. The present work further discusses the properties of a series of hydrogels obtained by free radical copolymerization of α,ω–methacryloyloxy poly(ethylene oxide) (PEO) or poly(1,3-dioxolane) (PDXL) macromonomers. The influence of several parameters such as macromonomer molar mass, comonomer concentration, solvent, and crosslinking concentration on the weight degree of equilibrium swelling, the uniaxial compression modulus and the thermodynamic interaction parameter was investigated systematically. Hydrogels, whose elastic chains are constituted of a short central PDXL block surrounded by two hydrophilic PEO blocks, were prepared according to the same strategy, and their degradability in the presence of triflic acid examined. Some thermal properties of the different PEO or PDXL networks or co-networks were discussed in the last section.

Experimental

Monomers, solvents, deactivating agents

1,3-Dioxolane (DXL), tetrahydrofuran (THF), methacrylic acid, methyl methacrylate (MMA), butyl methacrylate (BMA), styrene (S) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich, distilled before use and kept under argon. Triflic acid was protected from air and light. The polymerization and functionalization reactions were conducted in a tight reactor under a slight argon pressure.

Synthesis of macromonomers

PEO, PDXL and PEO-*block*-PDXL-*block*-PEO macromonomers were prepared as discussed in several previous publications [2-5]. They were characterized by SEC for molar mass determination on a WATER ASSOCIATES apparatus with a WATERS 401 refractive index detector. Microstyragel columns were used (length 60 cm and diameter 1 cm). The eluent was THF (elution rate 1 $\mathrm{ml.mn^{-1}}$). PEO standards were used for calibration. NMR (Brüker AC 200NS), UV spectroscopy (UV/Visible Shimadzu 2101 PC apparatus) and chemical titration were used in order to determine the average functionality of the different macromonomers.

Polymerization of macromonomers: hydrogel synthesis

The macromonomers were (co-)polymerized in water (or in THF in some cases) at 60 °C to networks. 2,2’-azobisisobutyronitrile (AIBN) and potassium peroxodisulfate were used as initiator in THF and in water, respectively (2 mol % versus double bond content). The gel point was reached after a few hours, and was dependent upon the chain length of the macromonomer precursor, its concentration and the nature of the solvent. The reaction was kept going for at least 24 h to use up the initiator. After preparation, the gels were kept either in the polymerization solvent, or exchanged with THF or water, for swelling.

Characterization of networks

The networks, free of linear unconnected chains, were characterized in terms of their swelling behavior according to well-established procedures. The measurements of the uniaxial compression modulus were made with a home built fully automated equipment as described elsewhere [2].

Differential Scanning Calorimetry

A Perkin Elmer microcalorimeter equipped with a thermal analysis station (TDADS) was utilized for DSC measurements. The linear precursors or the dry polymeric network or co-network samples, (around 25 mg), were introduced into sample pans which were then tightly sealed. Samples were dried (to constant weight) under vacuum at 50 °C during 3 days and cooled down under vacuum to room temperature. The sealed capsules were kept in a dessicator. The temperature was elevated at a rate of 10 °C min^{-1} and cooling was done at –2 or –5 °C min^{-1}.

Results and discussion

The main aim of the present work was to determine the influence of experimental parameters such as the average molar mass of the PEO or the PDXL macromonomer precursor, the concentration at which crosslinking takes place, the chemical nature of the comonomer (and its concentration), when the case, and/or the polymerization solvent (THF or water) on the physico-chemical characteristics of homo or copolymeric PEO or PDXL networks. The results were compared with theoretical expectations. Below are some remarks on these theories, useful for the interpretation of our results, will be given first.

Some theoretical considerations about networks

According to some authors crosslinking, which defines a macroscopic state of the networks, immobilizes the junction points. In this case, the positions of the junction points are affine to the macroscopic deformation leading to an affine relationship between strain and chain end-to-end vectors. If the junction points are allowed to fluctuate about their average positions, the so-called phantom model has to be considered [6]. Free energy of deformation can be represented by the so-called phantom network contribution and a term arising from topological interactions between the network chains (entanglement effect). For small strains, these topological interactions act as additional crosslinking points. The elastic moduli of the affine (G_{affine}) and phantom (G_{phantom}) models were established many years ago and are given below:

$$G_{\text{affine}} = \nu_e \mathrm{R} T \mathrm{v}_2^{1/3}\, \mathrm{v}_{2c}^{-1/3}$$

$$G_{\text{phantom}} = (\nu_e - \mu_e) \mathrm{R} T \mathrm{v}_2^{1/3}\, \mathrm{v}_{2c}^{-1/3}$$

Where ν_e and μ_e correspond to ν/V_0 and μ/V_0 and are the number of elastically active chains and the number of junctions per unit volume (V_0) in the nascent state, respectively (just before crosslinking), v_{2c} the polymer volume fraction of the gel after crosslinking but before swelling and v_2 is the polymer volume fraction of the swollen network. In most cases, the behavior of real networks can be described by including terms corresponding to partial suppression of junction fluctuations and by the contribution of physical entanglements, and therefore falls between the affine and the phantom limits.

Properties of swollen homopolymeric PEO or PDXL Networks

In previous publications [3, 4] we have shown that free radical homopolymerization of bifunctional PEO or PDXL macromonomers, when conducted at 60 °C in water, yields hydrogels in less than one hour. This result is attributed to the fact that, in aqueous medium, PEO (or PDXL) macromonomers (which contain a hydrophilic chain but hydrophobic polymerizable methyl methacrylate end-groups) are kept together by the aggregation of their ends (micellization). This self-organization is responsible for the enhanced polymerization rates in water. As in classical end-linking reactions [7, 8], each molecule of the crosslinking agent, the polymerizable entity attached at the chain end of the macromonomer should become a branch point connecting several chain ends. Each precursor chain becomes an elastically effective chain in the network as it connects two points of the infinite network. Whether such networks exhibit some structural defects such as loops, (one chain attached by its two ends to the same branching point) double connections (two branch points being connected twice) and loose chain ends, has still to be examined. Some characteristics data of PEO macromonomer based hydrogels are given in Table 1 below and Figure 1.

Table 1. Physico-chemical characteristics of PEO hydrogels obtained from PEO macromonomers: polymerization solvent: water.

Ref	M_n a)	[M] b)	ε (%) c)	$Q_{w,w}$ d)	$E_{g,w}$ e)
PEO1	2940	30	2.9	8.5	66000
PEO2	2940	45	4.2	6.85	122000
PEO3	2940	60	6.1	6.1	165000
PEO4	6150	10	4	15.1	16300
PEO5	6150	20	3.6	8.77	91300
PEO6	6150	30	3.8	6.98	129000
PEO7	6150	30	10.3	7.3	168000
PEO8	6150	45	3.4	6.6	183700
PEO9	6150	60	6.4	5.2	210000
PEO10	11500	10	4	20.1	12000
PEO11	11500	20	4	11.1	58300
PEO12	11500	30	9	8.79	116100
PEO13	20600	20	6.5	16.5	22500
PEO14	20600	30	3.8	13.8	56800

a) number average molar mass of the PEO macromonomer measured by UV (g.mol^{-1})
b) [PEO], %-wt. of macromonomer to be crosslinked
c) ε amount of extractable polymer in %-wt after 48 h
d) $Q_{w,w}$ weight equilibrium swelling degree measured in water
e) $E_{g,w}$ uniaxial compression modulus measured in water (Pa)

The detailed synthesis of these samples is given elsewhere [3, 9]. On the same Figure we added data on homopolymeric PDXL macromonomer based hydrogels whose synthesis and properties have been described in a previous paper [2].

From the results presented in Table 1 and Figure 1 following comments can be made: It is well established that the volume degree of equilibrium swelling is related to parameters, whos are experimentally accessible: the volume segment concentration upon crosslinking, v_{2c} and the average molar mass of the elastics chains. For most of our PEO hydrogels, the weight degree of equilibrium swelling in water (*Qw,w*) (Table 1 and Figure 1) increases with increasing molar mass of the macromonomer precursor chains. This result is interesting since it confirms that the pore size is indeed a function of the molar mass of the PEO macromonomer. In the case of our PDXL networks, the increase is much more pronounced in water than in THF. However, deviations from linearity are observed for networks constituted of precursors of low molar mass, below or around the critical entanglement molar mass (2500 $g.mol^{-1}$ for PDXL and 4400 $g.mol^{-1}$ for PEO, respectively).

To test the validity of the well-known equilibrium swelling equation, we examined the variation of the weight degree of equilibrium swelling as a function of M3/5. A linear evolution is observed, in good solvents, for the so-called model-networks, the structure of which is rather defined precisely concerning molar mass of elastic chains and functionality. Model-networks are obtained upon reaction of well-defined bifunctional precursors (the potential elastic chains) with appropriate low molar mass multifunctional coupling agents. Our networks were also prepared from well-defined precursors. The evolution of the weight degree of equilibrium swelling for PEO and PDXL macromonomers versus $M^{3/5}$ is presented in Figure 2. The linearity is confirmed unambiguously. Data on hydrogels made from precursors of molar masses around critical entanglement molar mass have been removed from plot for clarity.

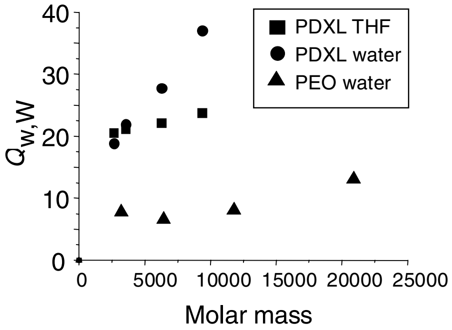

Figure 1. Evolution of $Q_{w,w}$ versus molar mass for PEO and PDXL networks. Square correspond to PDXL networks swollen in THF. [2, 3]

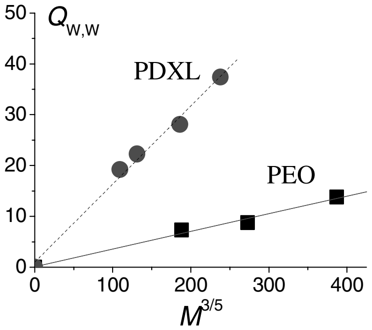

Figure 2. Evolution of $Q_{w,w}$ versus $M^{3/5}$ for PEO and PDXL networks whose precursor molar masses are above critical entanglement molar mass. [2, 3]

For a given molar mass of the precursor (except for the sample with precursor molar mass 2940 $gmol^{-1}$) the values of the uniaxial compression modulus of the hydrogel increase with increasing polymer concentration (see Table 1). This demonstrates that the density of elastically effective chains (governing the mechanical properties) is essentially influenced by the macromonomer concentration.

As expected, when the molar mass of the PEO chain rises from 6500 to 20500 $gmol^{-1}$, we observe a decrease in the compression modulus of the gel: Mechanical properties of the networks generally tend to be better for shorter precursor chains because of the higher density of crosslinking points. However, compression moduli measured for hydrogels obtained from precursors of molar mass around 3000 g.mol^{-1} are lower than the others. This result may be attributed to the absence of entanglements between PEO chains. According to Aharoni [10], the molar mass between entanglements (M_e) is around 4400 g.mol^{-1} for PEO. Thus, for a 2940 g.mol^{-1} molar mass PEO, only few entanglements are present, and the molar mass between the bridges is the molar mass of the PEO chain. For higher molar mass PEO chains, the probability of forming entanglements increases and the real "molar mass" between the crosslinking points is decreased by the existence of physical bridges between chains.

Additional information on the structural parameters can be obtained from the analysis of the E_g/Q correlation at equilibrium: E_g, prop. Q^{-m} where m is a parameter related to the number of elastic chains of the excluded volume theory $m = (1-1/3\nu)^{-1}$ $\nu = 3/5$ (good solvents), 1/2 in θ solvents and 1/3 in poor solvents, m = 2.25, 3.0 and infinite, respectively.

This well known scaling law was tested for our PEO or PDXL macromonomer based hydrogels. A typical representation is given in Figure 3. Theoretical curve for samples placed in a good solvent yields m = 2.25. The straight line drawn according to the experimental values is characterized by a slope of 2.5 for homopolymeric PEO networks whatever the concentration or the molar mass (Figure 3).

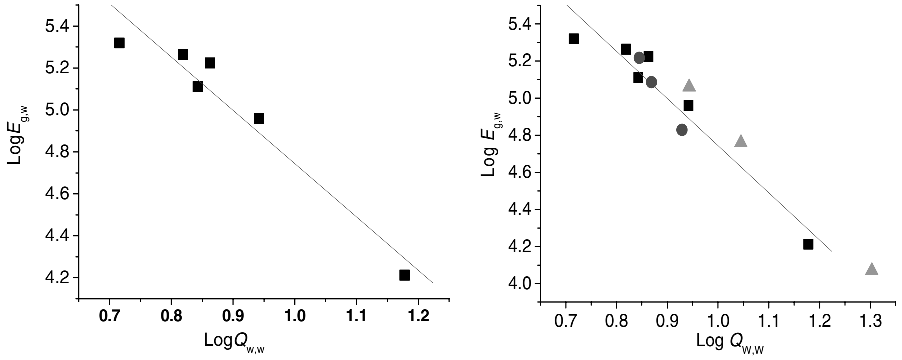

Figure 3. Bilogarithmic correlation plot of the uniaxial compression modulus measured in water (E_g) versus the weight degree of equilibrium swelling in water for PEO macromonomer based hydrogels (on the left versus concentration (molar mass precursor 6150 g.mol^{-1}, samples PEO 4-9, Table 1), (on the right versus precursor molar mass and concentration (Table 1) (circular points: M_n= 2950 g.mol^{-1}, triangles: M_n = 11500 g.mol^{-1}).

The small difference (2.25 / 2.5) may be attributed to the presence of the hydrophobic poly(methyl methacrylate) (PMMA) core. This confirms that water is a rather good swelling solvent for homopolymeric PEO hydrogels. These conclusions are consistent with observations made on PEO hydrogels obtained via other crosslinking processes, and also characterized by low contents of hydrophobic cores. However, higher values (around 3) were obtained co-networks characterized by the presence of much higher contents of hydrophobic species.

Properties of PEO or PDXL co-networks

PEO or PDXL-co-MMA networks are characterized by the presence of hydrophilic elastic chains and hydrophobic segments, the PMMA junction points. They swell in water and THF, and typically behave as amphiphilic networks [11, 12]. They swell in water to a lower extend than pure PEO or PDXL networks. The physico-chemical behavior of PDXL macromonomer based co-networks have been extensively discussed in a recent paper [4] and the main conclusions are summarized below: Whatever the comonomer content (BMA or S), the weight degrees of equilibrium swelling are lower in water than in THF. This is attributed to a stronger affinity of the PMMA junction points for THF (a good solvent of the PMMA chain) than for water. The differences are more pronounced for PDXL co-networks than for PEO co-networks [13]: PEO is well soluble in water at room temperature whereas PDXL solutions in water are characterized by the presence of aggregates which is translated into additional reversible crosslinking points. Consequently, weight equilibrium swelling degree values are lower than for PEO networks prepared at the same concentration and of identical precursor molar mass. For PEO co-networks whose elastic chains are constituted of long PEO chains, characterized by low contents of PMMA, weight degrees of equilibrium swelling are higher in water than in THF.

Mechanical properties of networks are known to be much more sensitive to small differences in structural parameters than equilibrium swelling degrees. This prompted us to examine, for the same PEO or PDXL co-networks, the evolution of the uniaxial compression modulus E_g with the ratio [MMA] / [PDXL] or [MMA] / [PEO]. For a given precursor molar mass, and for a given concentration, E_g (measured in water or in THF) increases with increasing MMA concentration. This result in not surprising since increasing MMA concentration, leads to the incorporation in the polymeric crosslinking points of higher amounts of MMA. Consequently, the functionality of the PMMA crosslinking point is increased, and the mechanical properties are improved. However, the behaviour is more complex for PEO co-networks characterized by much higher MMA contents [13].

Characterization of swollen PDXL-co-HEMA networks

For a given macromonomer concentration, the uniaxial compression modulus increases with increasing comonomer concentration. This behavior is somewhat similar to that of amphiphilic co-networks. In fact, PDXL-co-HEMA networks swell to a lower extend in THF than PDXL-co-MMA networks. Poly(HEMA) segments are not soluble in THF. For PDXL-co-HEMA networks swollen to equilibrium in water, $Q_{w,w}$ values are higher than for PDXL-co-MMA networks swollen to equilibrium in water. This is attributed to the fact that, even if water is a poor solvent of poly(HEMA), the poly(HEMA) noduli can swell in water. On the contrary, PMMA segments, constituting the noduli in PDXL-co-MMA networks, are not soluble at all.

Degradable PDXL or PEO-block-PDXL-block-PEO networks

PDXL chains are much more sensitive to the attack by an acid than PEO chains, and this should also be true for PDXL chains incorporated in a network structure. The evolution of the mechanical properties of macromonomer based PDXL networks, swollen to equilibrium in organic solvents in the presence of triflic acid, was studied as a function of time [2]. As expected the uniaxial compression modulus decreases with time, confirming the decrease of the number of the elastic chains in the network.

This decrease corresponds to the degradation of the PDXL chains. The evolution of the mechanical properties of PDXL networks placed in acidic medium is directly connected to the length of the elastic chains: For a given reaction time, the uniaxial compression modulus decreases much more rapidly for longer precursor chains. This result is not surprising. This degradation reaction was also examined for PDXL or PEO-*block*-PDXL-*block*-PEO networks swollen to equilibrium in water. Contrary to that is observed by Goethals [14] degradation takes place also in water. The evolution, versus immersion time, of the number of elastically effective chains was followed by uniaxial compression modulus measurements and by solid-state ^{1}H NMR spectroscopy [15].

Thermodynamic interaction parameters of PEO, PDXL or PEO, PDXL co-networks

PEO or PDXL co-networks originating from the same macromonomer precursor, prepared at the same concentration, but characterized by differences in comonomer contents in their noduli, or networks synthesized at the same macromonomer concentration and comonomer content, but made from different precursors behave differently. This was concluded from the evolution of data on the weight degree of equilibrium swelling and on the uniaxial compression modulus. Therefore, it is assumed that the interaction parameter χ_{12} of the swelling solvent with the crosslinking point may be different from that of the linear chain elements (elastic chains), and may also change with the macromonomer molar mass, its concentration, the functionality of the crosslinking point, the comonomer content or type. The interaction parameter χ_{12} between the swelling solvent and the PDXL co-networks can be calculated using following equation in which all parameters are known.

$$\ln(1-v_2)+\ v_2+v_2{}^2x_{12}=-\frac{V_1}{V_0}\frac{E_g}{RT}v_2c^{1/3}$$

Some results on PDXL co-networks are discussed in the following. The interaction parameter values for all homo or co-MMA PDXL networks, swollen to equilibrium in water, are higher than for the same networks swollen to equilibrium in THF. The hydrophobic nature of the polymeric crosslinking agent is clearly evidenced. Poly(MMA) in well soluble in THF, but not soluble in water. This confirms the evolution observed for equilibrium or uniaxial compression measurements. χ_{12} is higher for PDXL co-MMA networks swollen to equilibrium in water or in THF, than for the homopolymeric PDXL networks. This can be explained by the higher amount of PMMA junction points characterizing the copolymeric networks. Whatever the swelling solvent and the nature of the PDXL network (homopolymeric, copolymeric containing hydrophilic or hydrophobic comonomers) χ_{12} is a linear function of v_2, the volume fraction of polymer in the swollen state. These results are consistent with investigations made on linear polymers or on PEO or PDXL networks prepared by end-linking reactions establishing χ_{12} to be concentration dependent. The case of PDXL-co-HEMA networks is also of interest. For low volume fractions of polymer, corresponding to low comonomer contents, χ_{12} values calculated in THF are higher than χ_{12} values calculated in water. Contrary to PMMA, poly(HEMA) is not soluble in THF, and precipitates as soon as it is formed. Therefore the presence of the poly(HEMA) cores in PDXL-co-HEMA networks, leads to an increase of the thermodynamic interaction parameter in THF compared to pure PDXL networks or to PDXL-co-MMA networks. In THF, χ_{12} values do not change with increasing volume fractions of polymer whereas, in water, χ_{12} increases rapidly with increasing volume fractions of polymer. These results are self-consistent with the behavior of homo-or copolymeric poly(HEMA) hydrogels in water. As mentioned previously, water is thermodynamically poor solvent for poly(HEMA). Therefore changing HEMA content, should change the value of the thermodynamic interaction parameter in water.

Differential Scanning Calorimetry studies

In the following, some aspects of the crystallization of homopolymeric PEO, PDXL or PEO-*block*-PDXL-*block*-PEO networks will be discussed on the basis of DSC results, in order to access thermodynamic parameters such as phase changes, melting and crystallization temperature, and to determine the consequences of crosslinking on these processes. The influence of the presence of hydrophilic or hydrophobic comonomers on the overall crystallization behavior will also be examined. The solid-state properties, in direct relation with the crystallization potentiality and /or crystalline structures of PEO, or of poly(methylene oxide), POM or PEO, have been widely studied. PDXL is a perfectly alternating copolymer made of units constituted of POM and PEO. Crystalline behavior of water-PEO [16] or water-PDXL systems of various molar masses and composition were examined previously [17].

The glass transition temperature (T_g) values of linear chains are almost constant corresponding to values around –55 °C for PEO (for molar masses higher than 6000 g.mol^{-1}) and – 56 °C for linear PDXL of molar mass around 10000 g.mol^{-1}. T_g values (Table 2) measured for crosslinked PEO or PDXL chains are slightly higher than those corresponding to free PEO or PDXL chains. This is attributed directly to cross-linking, most of the chain ends being connected to the network structure, implying a strong limitation of there mobility.

Table 2. Calorimetric data for PEO, PDXL or PEO-*block*-PDXL-*block*-PEO networks

Ref	M_n (g/mol)	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_f (J/g)
PEO	2500	-52.6	15.3	47.1	93.59
PEO	6000	-50.0	22.2	62.0	130.64
PEO	11500	-50.5	29.5	59.7	-
PDXL	2500	-56.2	-	-	-
PDXL	3400	-56.3	-	-	-
PDXL	9200	-58.9	-	-	-
PEO-PDXL-PEO	6000	-56.5	1.1	37.5	61.64
PEO-PDXL-PEO	17600	-54.0	35.5	58.6	120.44

The melting point (T_m) value of linear PEO chains is close to 60 °C (for molar masses higher than 5000 g.mol^{-1}). This value is not too different from that measured for the PEO networks. For PDXL homopolymers only one melting peak is observed, between 46.1 and 51.8 °C (PDXL 2300 g.mol^{-1}), 41.3 and 56.3 °C (PXDL 6000 g.mol^{-1}) and between 43.4 and 51.8 °C (PDXL 9200 g.mol^{-1}). The situation is more complex once crosslinked. Two peaks appear for the high molar mass samples, between 59.2 et 63.3 °C and 26.6 et 43.7 °C. For the low molar mass sample (3400 g.mol^{-1}), only one melting peak is observed, between 28.05 et 28.30 °C. Crystallization temperature also changes with macromonomer chain length. For a given molar mass, increasing macromonomer concentration corresponds to a decrease of the melting temperature, related probably to a lower crystallinity of the system. Further work has to be made to clarify the situation.

The same studies were performed on PDXL co-networks [4]. As for homopolymeric networks, the values are slightly higher than those corresponding to free PDXL chains. For a given comonomer concentration, increasing the macromonomer concentration, leads to a decrease of the melting temperature, corresponding to a lower crystallinity. Increasing comonomer concentration (at constant macromonomer molar mass and concentration) does not affect too much melting and crystallization temperature. The case of MMA is much more interesting: for a dry hydrogel obtained by copolymerization of a PDXL macromonomer of molar mass 2500g.mol^{-1}, no crystallization at all is observed by DSC. Similar observations were made by Goethals. A possible explanation may be the high rigidity of the PMMA backbone which limits the flexibility of the PDXL chains and prevents them from crystallizing. When the length of the PDXL precursor is increased, crystalline domains are again present.

In order to determine the influence of the presence of poly(HEMA) segments on the solid-state properties, we submitted also PDXL-co-HEMA networks to DSC characterization. The results are almost similar to those obtained for PDXL-co-MMA networks. Glass transition temperatures are higher than for linear PDXL samples and do not change significantly with increasing comonomer content. For the sample of precursor molar mass 2500 g.mol^{-1} the behavior is comparable to the PDXL-co-MMA case, no crystallization is observed. The explanation is the same. However, PDXL-co-HEMA networks are characterized by higher macromonomer molar mass present crystalline domains.

Conclusions

PEO or PDXL networks could be obtained directly in water by copolymerization of well-defined macromonomers with low molar mass comonomers. The parameters influencing the reaction were examined systematically. Among these, the molar mass of the polymer precursor and the overall concentration of the reaction mixture are the key parameters. In addition, it has to be underlined that, increasing concentration of hydrophobic comonomer, leads to improved mechanical properties. The Flory-Huggins interaction parameters were determined both in water and organic solvents. The results were confirmed by the investigation of their solid-state properties.

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