For MCA, a slight rise of $\bar{M}_w$ with increasing conversions is found, which, at 110 °C, may be explained by transfer to polymer with $C_p = 5 \times 10^{-4}$ per monomer unit (i.e., non end group). For CEMA, transfer constants to some solvents were also determined.

solvent	$C_s^{60\,°C}$
CCl_4	3.27×10^{-5}
$CHBr_3$	1.68×10^{-4}
C_6H_5SH	232

Conclusions

The results presented in this paper show that besides the external heavy-atom effect by solvents or inert gas on the spontaneous polymerization of MMA discussed in the previous paper, an internal effect by chlorine substitution can be observed. As in the spectroscopy of naphthalenes (Table I), the internal effect is much more pronounced.

The reaction orders, the dependence on the atomic number of the heavy-atom included internally or externally, and the parallels to the spectroscopic results strongly support the interpretation of a heavy-atom catalysis of intersystem crossing. This implies that the multiplicity change of the originally formed singlet biradicals is of reasonable importance for the initiation step of the polymerization of MMA and related compounds.

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Registry No. Methyl α-chloroacrylate, 80-63-7; β-chloroethyl methacrylate, 1888-94-4; poly(β-chloroethyl methacrylate), 26937-47-3; methyl methacrylate, 80-62-6; ethyl methacrylate, 97-63-2; poly(ethyl methacrylate), 9003-42-3; poly(methyl α-chloroacrylate), 25704-33-0.

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Hydrophilic Polyurethane Networks Based on Poly(ethylene oxide): Synthesis, Characterization, and Properties. Potential Applications as Biomaterials[†]

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ABSTRACT: Hydrophilic polyurethane networks have been synthesized by step growth polymerization between poly(ethylene oxide) precursor polymers and suitable aliphatic or aromatic pluriisocyanates. The reactions have been carried out in organic solvents such as dioxane. The quantitative exchange between dioxane and water yields optically transparent hydrogels of high hydrophilicity exhibiting improved mechanical properties. The final structure of the networks and their ultimate properties depend upon several parameters such as the type of the pluriisocyanate used, the number-average molecular weight, and the concentration of the precursor poly(ethylene oxide) as well as its polydispersity. The solvent, the temperature, and the catalysts influence considerably the rate and the total duration of the process. The networks obtained are characterized by their equilibrium swelling degrees in dioxane and in water and by their elastic moduli arising from uniaxial compression measurements. In most cases, the materials obtained are optically perfectly transparent, highly hydrophilic with satisfactory mechanical properties, and therefore suitable as potential biomaterials.

Introduction

The numerous methods which have been developed to synthesize hydrophilic polymer networks can be classified into three groups: (1) methods involving free radical copolymerization of two monomers, one of them being biunsaturated and present in small proportions (e.g., 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (DME)[1-4]); (2) methods involving graft copolymerization (e.g., graft copolymers of poly(HEMA) onto poly(vinylpyrrolidone)[5] or poly(vinylpyrrolidone) onto silicone rubber[6]); and (3) methods involving step growth polymerization between preexisting linear polymer chains and an appropriate functional reagent (e.g., reaction between an α,ω-dihydroxy polymer and a pluriisocyanate[7]

[†] Dedicated to Professor W. H. Stockmayer on the occasion of his 70th birthday in grateful recognition and with best regards.

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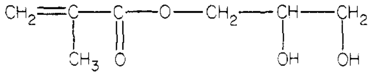
(compounds containing three or more isocyanate functions are referred to as "pluriisocyanates")).

The use of hydrophilic polymer networks as biomaterials has been extensively developed since the pioneering work of Wichterle and Lim.[1,8] Around 1960, these authors established that hydrogels synthesized from methacrylic esters containing at least one alcohol group per monomer unit are potentially efficient as biomaterials[9] in orthopedic surgery, as plastic implants, and chiefly as soft contact lenses, owing to their good biocompatibility. Well-fitting materials have been obtained by free radical copolymerization of 2-hydroxyethyl methacrylate with a biunsaturated monomer such as ethylene dimethacrylate.[1] These materials have been applied with great success to manufacturing soft contact lenses[8] that exhibit adequate biocompatibility and satisfactory optical properties. However, transparent and homogeneous materials are obtained only if the water concentration at the gel point is less than 40%, whatever the cross-linking density may be: it was shown that the maximum swelling degree of poly(HEMA) hydrogels is limited by thermodynamics.[10] If higher water contents are present in the reaction medium, the excess of diluent is expelled from the gels:[11,16] syneresis takes place, leading to opaque, heterogeneous, macroporous, spongy materials exhibiting poor mechanical properties. Transparent swollen hydrogels with less than 40% water exhibit insufficient permeability to oxygen to allow adequate epithetial respiration, especially if the eyelids are closed.[12] In spite of these disavantages poly(HEMA) hydrogels are still the biomaterials most commonly used as soft contact lenses.

Since 1976, in the Centre de Recherches sur les Macromolécules at Strasbourg, research has been carried out in the field of hydrophilic polymer networks, aiming at the synthesis and the characterization of biocompatible hydrogels exhibiting better hydrophilicity and improved mechanical properties with respect to poly(HEMA) hydrogels. The first attempts have been performed by Hild[13] using 2,3-dihydroxypropyl methacrylate (DHPM), a monomer fitted with two hydroxy groups in the side chain:



$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH(OH){-}CH_2(OH)$$

DHPM is more hydrophilic than HEMA. It has been prepared by an original method[14] and yields hydrogels of large hydrophilicity. More recently, Macret and Hild[10] have investigated the synthesis of hydrogels, starting from various mixtures of pure HEMA and DHPM[15] and using DME as cross-linking agent. The free radical copolymerization of this ternary system leads to materials, the hydrophilicity of which increases as the proportion of DHPM increases. Syneresis sets in above 90% water for poly(DHPM) networks instead of 40% for poly(HEMA) gels of similar cross-link density. On the other hand, when swollen to the same extent, materials containing DHPM exhibit elastic moduli higher than those of poly(HEMA) hydrogels.

Table I
Determination of the Density d_0 of the Dry Gel

sample	M_n[a]	M_w/M_n[b]	X[c]	d_0[d]
PEO1000S	1010	1.07	0.666	1.161
PEO2000S	1810	1.07	0.784	1.179
PEO4000S	3400	1.05	0.870	1.191
PEO6000S	5650	1.06	0.917	1.198
PEO10000S	8250	1.10	0.942	1.201

[a] From OH titration by phosgenation. [b] From the GPC diagrams. [c] Fraction of PEO in the dry sample. [d] Density of dry gel.

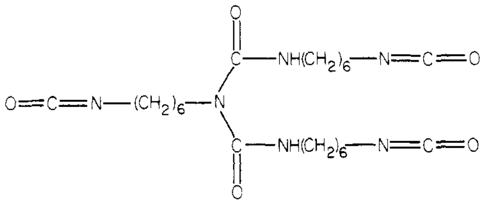
The present work deals with the synthesis of hydrogels by step growth polymerization in an organic solvent. The reaction involves a hydrophilic precursor polymer fitted at both chain ends with alcohol functions and an appropriate pluriisocyanate. Under well-defined experimental conditions, such a process should lead to hydrophilic polyurethane networks. Step growth polymerizations have been used widely to synthesize networks.[7] Poly(propylene oxide) (PPO) serves often as precursor in polyurethane chemistry: hydrophobic polymer networks have been obtained and their properties have been studied by several investigators[17-20] to test the validity of the current thermodynamic theories.[21,22] The use of poly(ethylene oxide) as precursor chains has been mentioned in a few papers.[23-25] It is established that poly(ethylene oxide) exhibits a good biocompatibility and even a satisfactory blood compatibility:[27] Polyurethanes based on poly(ethylene oxide) have the lowest platelet retention factors of all similar polyether-based polyurethanes, as shown by Merrill.[26,27] These materials have been considered for some biomedical applications[28,29] but, to our knowledge, they have not been selected for use in soft contact lenses.

Experimental Section

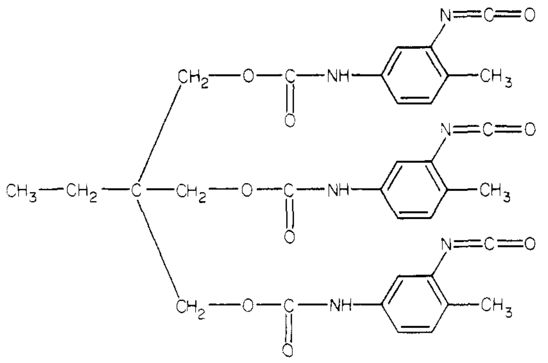
Materials. Hydroxy-Terminated Poly(ethylene oxide) (PEO). The PEO samples employed were generously supplied by Hoechst Co. as PEO1000S, PEO2000S, PEO4000S, PEO6000S, PEO10000S, and PEO20000S, designations that indicate their approximate molecular weights. Each PEO sample was dissolved in benzene, precipitated from ether at 10 °C, and dried. To remove the last traces of water, the polymer was redissolved in 4 volumes of dry distilled benzene and freeze-dried just before its use. The water content was found by Karl Fischer titration to be less than 0.01%. The number-average molecular weights M_n were determined by size exclusion chromatography (GPC) using anhydrous tetrahydrofuran as the elution solvent. Simultaneously, hydroxy end group analysis was carried out by phosgenation followed by hydrolysis and back-titration of the chloride ions formed as described in the literature.[30] The values of M_n are listed in Table I.

Trimethylolpropane (TMP) supplied by Bayer was recrystallized and its purity was found to be satisfactory.

Isocyanates. Hexamethylene diisocyanate (HMDI) supplied by Aldrich was purified by fractional distillation and kept under anhydrous conditions at low temperature and in the dark. Pluriisocyanates (Desmodur N75 and Desmodur L) were kindly provided by Bayer. Their "ideal" formulas were the following:



Desmodur N75



Desmodur L

Kept under dry argon, they remain stable for at least 6 months. They were used without further purification after titration with di-*n*-butylamine.[31] Our results showed that the average functionality f is higher than expected from the above formulas.[32] To get the exact value of f of these pluriisocyanates, we prepared anionically a PEO sample of known molecular weight containing *one* hydroxy group[33] at the chain end. The pluriisocyanate was mixed in stoichiometric amount with the monofunctional PEO, the reaction being carried out for 48 h at 60 °C to avoid side reactions. After precipitation and drying, the weight-average molecular weights M_w of both the initial and the "star" polymers were determined by light scattering in methanol solution. The following values were found: $M_w = 2100$, initial monofunctional PEO; $M_w = 13\,600$, after reaction with Desmodur N75; $M_w = 15\,500$, after reaction with Desmodur L. Thus the functionality of the pluriisocyanate is between 5 and 6 for Desmodur N75 and between 6 and 7 for Desmodur L if account is taken of the contribution of the pluriisocyanate to the overall molecular weight. This result contradicts previous statements of Pinazzi et al.[34]

Solvent. The solvents used (dioxane, tetrahydrofuran, xylene, dimethylformamide, ethyl acetate, dichloroethane, and *N*-methylpyrrolidone) were made free of water[35] and kept under dry argon prior to their use.

Catalysts. Diazabicyclo[2.2.2]octane (Dabco) and triethylamine were used without further purification.

Experimental Procedure. The synthesis of hydrophilic PEO networks was performed by the following general procedure. After freeze-drying of the PEO precursor polymer in the reaction vessel, the solvent (generally dioxane) and the pluriisocyanate (aliphatic or aromatic) were mixed in stoichiometric proportions ([NCO]/[OH] = 1) under dry argon, generally in the absence of catalyst. This mixture was then transferred under an anhydrous atmosphere into glass tubes, each containing a cylindrical mold made of polyethylene. After three degassings, the tubes were sealed off and kept under vacuum at a constant temperature (generally 60 °C) in a thermostat for the desired time (generally about 1 week). The gels formed were then removed from the molds and placed into an excess of dioxane to allow them to reach their equilibrium swelling state.

To determine the sol fraction, the dioxane was replaced every other day over a 3-week period until no further extractable polymer could be detected. The amount of soluble polymer in the gel was determined gravimetrically after evaporation of the solvent. From the characterization by GPC in THF it was found that the extracted PEO exhibits at least the molecular weight of the PEO precursor used.

In order to obtain water-swollen networks, two methods were used: (i) either the material swollen in dioxane was slowly dried at 25 °C to constant weight and then reswollen in water to its equilibrium swelling degree or (ii) a slow solvent exchange was performed (replacing dioxane by water), whereby much care is required: the water content of the swollen network has to be increased very slowly in order to prevent the osmotic forces from destroying the hydrogels. In both cases, transparent homogeneous hydrogels were obtained.

Equilibrium Swelling Degree. The method of determination of the equilibrium volume swelling degree Q of the networks has already been described in several previous papers.[11,13] The Q values are calculated from the equilibrium weight swelling degree G using the equation

$$Q = 1 + (G - 1)(\bar{d}_0/\bar{d}_s)$$

$\bar{d}_s$ and $\bar{d}_0$ being the densities of the solvent ($\bar{d}_s = 1.03$ for dioxane) and of the dry gel, respectively. Depending upon the proportions of pluriisocyanate in the initial mixture, the density of the dry network can be calculated from the densities of the reagents (i.e., $d_{\mathrm{PEO}} = 1.21$ and $d_{\mathrm{DN\ 75}} = 1.08$) using the equation

$$\bar{d}_0 = X d_{\mathrm{PEO}} + (1 - X)\bar{d}_{\mathrm{D\ N75}}$$

where X is the proportion by weight of PEO in the network. The values of d_0 are gathered in Table I. The polymer concentration C_e at equilibrium is given[36] by

$$C_e = \bar{d}_0/Q$$

It is sometimes useful to express the solvent content T in the swollen material[10,12] as

$$T\,(\%) = \frac{P_{sw} - P_d}{P_{sw}} \times 100 = \frac{G - 1}{G} \times 100$$

P_{sw} and P_d being the weights of the sample in the swollen and in the dry state, respectively.

Elastic Modulus. The values of the elastic moduli E_G in the swollen state were obtained from uniaxial compression measurements using an apparatus similar to that described by van de Kraats[37] and by Dondersloot et al.[38] The compression measurements were carried out as described previously,[10,11,13] If A_{sw} is the base area of the swollen cylinder of gel, the reduced force is given by[39]

$$F/A_{sw} = ART\nu_e Q^{-1/3} h^{2/3}(\lambda - \lambda^{-2})$$

where A is a constant, ν_e is the number of elastic chains per unit volume of swollen gel, λ is the deformation ratio, and h is the so-called "memory term", first introduced by Dusek and Prins.[39] From the experimental values of F, A_{sw}, Q, and λ the elastic modulus results:

$$E_G = \frac{\sigma}{\lambda - \lambda^{-2}} = ART\nu_e h^{2/3} Q^{-1/3}$$

All measurements of the force F have been performed instantaneously: they take into account neither possible volume changes nor relaxation phenomena.

Results and Discussion

Synthesis of the Cross-Linked Poly(ethylene oxide) Hydrogels. Preliminary experiments have shown that upon reaction of a precursor poly(ethylene oxide) (PEO) carrying alcohol functions at both chain ends with a pluriisocyanate, highly hydrophilic materials are obtained. However, to get a good reproducibility the presence of trace amounts of water in the PEO has to be prevented. That is why the special drying procedure described in the Experimental Section was used in all further syntheses.

Several methods have been utilized for the preparation of the networks as shown below:

Network Formation by Reaction of PEO with Pluriisocyanate. This method is based upon the reaction of a poly(ethylene oxide) precursor of known molecular weight M_n with a pluriisocyanate (aliphatic or aromatic) or well-characterized average functionality f. When such end-linking processes are carried out under conditions of exact stoichiometry [OH]/[NCO] = 1 with purified reagents and in the presence of a suitable solvent (such as dioxane), the networks obtained exhibit satisfactory homogeneity. Structural defects, such as loops or double connections, are generally few, except when the overall concentration is very low.[40-42] It is essential to carry out the reaction to very high conversion in order to drastically reduce the proportion of dangling chains.

This method was used to synthesize networks starting from poly(ethylene oxide) precursors of molecular weights M_n = 1010, 1810, 3400, 5650, 8250, respectively. The concentration of PEO in dioxane solution was chosen as to cover a broad range, extending from 5% to 60% by weight, and a few additional experiments were carried out in the bulk.

In most cases, the gel points were reached after a few hours of reaction, the conversion degrees being still quite low. The duration of the reaction that is required to obtain networks with negligible amounts of extractable polymer still depends on the experimental conditions chosen.

Network Formation Using a Triol as Cross-Linker. This method, frequently used in polyurethane chemistry,[18] was also applied to the synthesis of hydrogels derived from PEO precursor chains. The PEO was reacted with hexamethylene diisocyanate (HMDI) in the presence of tri-

Table II
Influence of the Duration of the Reaction on the Characteristics of the Gels Swollen at Equilibrium in Dioxane[a]

t, h	% ex	Q	$C_e \times 10^2$	T, %	$E_G \times 10^{-5}$
No Catalyst (t_c = 18 h)					
20	35.4	28.06	4.28	95.75	0.485
31	30.6	25.75	4.66	95.30	0.877
55	16.5	19.30	6.22	93.84	1.520
79	11.5	16.31	7.36	92.73	2.146
103	7.5	14.38	8.34	92.14	2.736
168	2.2	12.84	9.35	91.07	4.320
0.1% Dabco (t_c = 6 h)					
48	0.4	8.46	14.18	86.54	11.50

[a] C_{PEO} = 33%, M_n = 5650, T = 60 °C. t, duration of the reaction; t_c, time after which gelification occurs (gel point); % ex, extractable polymer fraction; Q, equilibrium volume swelling degree; T, dioxane content in the swollen gel; E_G, elastic modulus (dyn/cm^2); C, weight concentration of PEO precursor.

methylolpropane. The amount of triol was chosen such as to fulfill the following conditions:

$$[OH]_{PEO} = [OH]_{TMP}$$

$$[NCO] = \tfrac{1}{2}[OH]_{PEO} + \tfrac{1}{2}[OH]_{TMP}$$

which imply exact overall stoichiometry.

The reactions were carried out with the same PEO samples (1010 < M_n < 8250) at an overall concentration of 33% by weight in dioxane. Transparent homogeneous networks were obtained by this method as well.

Network Formation Involving "Chain Extension". The chief aim of these syntheses was to establish whether an increase of the polydispersity of the network chains would influence the optical and the mechanical properties of the hydrogels formed. It should be recalled that the PEO precursors used in this work exhibit narrow molecular weight distributions.

Chain extension reactions are in fact polycondensation processes that result in an increase of the molecular weight but also in a marked broadening of the molecular weight distribution.

A precursor PEO of molecular weight 1810 is reacted with HMDI as chain extender. Thereafter the aliphatic pluriisocyanate is added to an amount calculated as to get exact stoichiometry. The reaction finally yields homogeneous networks.

This reaction can also be carried out in one step: a mixture of PEO, HMDI, and Desmodur N75 is reacted in dioxane for 1 week, the proportions of reactants being the same as above.

Characterization Results. The step growth polymerization process yielding poly(ethylene oxide) networks is influenced by a number of factors: structure of the pluriisocyanate, number-average molecular weight M_n of the PEO precursor, concentration, temperature, nature of the solvent, and presence and amount of catalyst. These factors influence the rate of the process and, especially, the time t_c after which cross-linking sets in (gel point). The influence of these parameters on the equilibrium swelling degrees and on the elastic moduli of the swollen networks will be discussed as well.

Duration of the Reaction. We have determined the amount of extractable polymer in the networks as a function of the reaction time. Starting from a precursor PEO of M_n = 5650 at a concentration of 33% in dioxane reacted with the aliphatic pluriisocyanate in the absence of a catalyst, the gel point is reached after 18 h. Reaction times ranged from 20 to 168 h, and each of the networks was thoroughly extracted with dioxane for 3 weeks. Thereafter no further chains could be extracted.

Table III
Characterization of Gels Swollen at Equilibrium in Dioxane at a Temperature of 80 °C[a]

t,[b] h	% ex	Q	$C_e \times 10^2$	T, %	$E_G \times 10^{-5}$
6	25.6	52.11	2.30	97.78	0.214
7	18.2	28.87	4.16	96.00	0.812
9	7.25	18.57	6.46	93.80	1.75
24	4.1	13.31	9.02	91.38	3.00
168	0.8	10.95	10.96	89.55	5.84

[a] C = 33%, M_n = 5650. [b] t_c = 5.50 h.

As expected, the fraction of extractable polymer decreases as the reaction time increases (Table II). The swelling degrees of the networks (after extraction) also decrease, and the moduli increase appreciably as the duration of the reaction increases. This shows that care should be taken in any further comparison to deal with samples that have been reacted to very high conversion.

Influence of Catalysts. PEO networks were obtained as above (with Desmodur N75 at 60 °C in dioxane at c = 33% by weight), but in the presence of either triethylamine or diazabicyclooctane (Dabco) as catalysts. The efficiency of these compounds in urethane formation is well-known.[7] They can be removed quantitatively from the gel during the extraction procedure. With 0.1% by weight of these catalysts, the gel point is reached after 11 h with triethylamine and after 6 h with Dabco, instead of 18 h in the absence of catalyst.

As can be seen from Table II the degree of conversion attained in the presence of 0.1% Dabco after 48 h of reaction is higher than that reached after 1 week in the absence of catalyst: the amount of extractable polymer is less, the swelling ratio is smaller, and the modulus is far higher.

Reaction Temperature. Most of the reactions were carried out at 60 °C. The rate increase that results from a rise of the reaction temperature from 60 to 80 °C is evidenced by the data shown in Tables II and III, which refer to the same precursor, the same concentration, and the same pluriisocyanate (in the absence of catalyst). The gel point is observed after 5.5 h (instead of 18 h at 60 °C). The fraction of extractable polymer is lower, the swelling ratio is smaller, and the modulus is higher for any given reaction time when the process is carried out at a higher temperature. The gels obtained are homogeneous and transparent.

In spite of these results, most of the network syntheses were carried out at 60 °C, a temperature at which allophanate linkages are unlikely to be formed.

Influence of the Solvent. Preliminary experiments were performed in xylene and in toluene. The networks obtained exhibited rather poor optical properties, especially when the precursor polymer had a molecular weight higher than 2000. This originates from the fact that xylene is a "bad" solvent for PEO.

Dioxane, being miscible with water and a "good" solvent for PEO, was found to be well suited for the synthesis of hydrophilic polyurethanes based on poly(ethylene oxide) precursors. The exchange between dioxane and water can be performed directly, without any intermediate drying, and homogeneous transparent networks are obtained in most cases.

Several other anhydrous solvents have been tested: dimethylformamide, tetrahydrofuran, ethyl acetate, N-methylpyrrolidone, and dichloroethane. Comparative experiments were carried out at 60 °C using a PEO precursor of M_n = 1810 at a concentration of 33% with a

Table IV
Influence of the Solvents Used on the Appearance of the Gel Point t_c[a]

solvent used	ϵ	β	t_c, h
dimethylformamide	36.71	0.69	7
N-dimethylpyrrolidone	32	0.71	8
tetrahydrofuran	7.58	0.55	10
ethyl acetate	6.02	0.45	11
dioxane	2.21	0.37	12
dichloroethane	10.0	0	20

[a] t_c, gel point; ϵ, dielectric constant of the solvent; β, parameter characterizing the acceptor effect of the hydrogen bond.

stoichiometric amount of the aliphatic pluriisocyanate. The times t_c necessary to reach the gel point range from 7 (in DMF) to 20 h (in dichloroethane) (Table IV).

The rate of the reaction between isocyanate and alcohol is known to depend upon both the dielectric constant ϵ of the solvent and the nucleophilic character of the alcohol;[43] a precise description of the solvent effect on chemical processes using only the dielectric constant is questionable.

As an example, one can mention the reaction rates of diols with diisocyanates, which are larger in toluene than in dioxane, even though these two solvents exhibit quite similar ϵ values.[44] In a more rigorous approach, Kamlet et al.[45] suggested that in addition other types of solute–solvent interactions should be taken into account, namely, the hydrogen bond accepting power β. Such a parameter is useful in understanding the difference of reaction rates in solvents having similar dielectric constants ϵ. In Table IV the values of ϵ and β are gathered together with those of t_c. As expected, the t_c values show roughly the dependence of the reaction rate on both ϵ[35] and β[46] (except for dichloroethane), which allows us to classify the solvents tested according to their effect on the reaction rate: DMF > *N*-methylpyrrolidone > THF > ethyl acetate > dioxane.

Influence of the Number-Average Molecular Weight of the Poly(ethylene oxide) Precursor. The mechanical properties of polymer networks are known to depend on the length of the elastically effective network chains. This has been clearly demonstrated upon studying the properties of networks obtained by end-linking processes.[11,47,48]

Identical conclusions can be drawn from the data shown in Table V. The gels obtained contain less than 2.5% extractable polymer, and they are always homogeneous and optically transparent when swollen in dioxane or in water. The values of the equilibrium swelling degrees Q and of the elastic moduli E_G (upon uniaxial compression) were measured in both solvents.

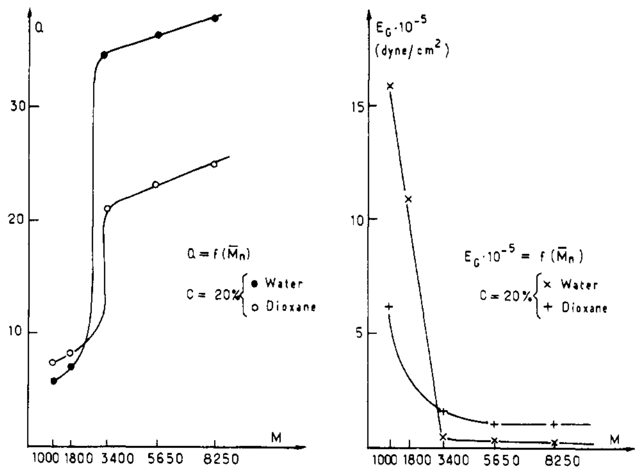


Figure 1. Equilibrium swelling degree and the elastic modulus shown as a function of molecular weight of the network chains.

For each series of networks, the values of Q increase and the values of E_G decrease as the molecular weight of the precursor increases. However, rather large differences are induced by the nature of the swelling solvent, as shown in Figure 1: water is a better swelling solvent than dioxane for networks with longer elastic chains ($M_n > 2000$). The reverse is true for networks with short elastic chains ($M_n < 2000$). This behavior probably originates from the hydrophobic character of the aliphatic urethane linkages, the proportion of which is higher in networks exhibiting shorter PEO chains.

Influence of the Overall Concentration of the Reaction Mixture. The data of Table V already indicate that the higher the overall concentration of the reaction medium for a given precursor polymer, the higher the modulus and the lower the equilibrium swelling degree of the networks obtained. More detailed results are displayed in Tables VI–VIII over a wide range of concentrations.

All these experiments were carried out with the aliphatic pluriisocyanate (in stoichiometric amount) in dioxane at 60 °C, the reaction times extending for several weeks.

Table V
Influence of the Molecular Weight M_n of the PEO Precursor on the Characteristics of the Gels at Equilibrium in Dioxane and in Water (T = 60 °C)[a]

				dioxane			water		
sample	M_n	C, %	% ex	Q	T, %	$E_G \times 10^{-5}$	Q	T, %	$E_G \times 10^{-5}$
PEO1000S	1010	20	2.1	7.50	85.0	6.16	5.93	80.9	15.8
PEO2000S	1810	20	2.1	8.28	86.4		7.16	83.9	10.9
PEO4000S	3400	20	5.3	21.04	94.5	1.65	34.64	96.6	0.38
PEO6000S	5650	20	5.2	23.17	95.0	1.01	36.36	96.7	0.25
PEO10000S	8250	20	3.4	25.00	95.2	1.05	57.47	96.8	0.20
PEO1000S	1010	33	2.4	5.66	80.0	17.02	4.35	74.3	19.8
PEO2000S	1810	33	1.3	7.76	85.5	11.6	6.56	82.0	12.7
PEO4000S	3400	33	1.5	13.26	91.3	5.07	15.10	92.2	2.98
PEO6000S	5650	33	2.2	12.84	91.0	4.32	15.54	92.3	2.15
PEO10000S	8250	33	5.1	15.80	92.6	3.25	20.33	94.2	2.56
PEO1000S	1010	50	1.6	4.84	77.0	22.0	3.94	71.0	24.9
PEO2000S	1810	50	0.5	5.28	79.0	26.5	4.96	77.0	23.3
PEO4000S	3400	50	1.7	9.45	88.0	7.87	10.34	86.6	6.38
PEO6000S	5650	50	1.8	10.45	89.0	6.14	13.26	91.0	3.45
PEO10000S	8250	50	1.3	13.00	91.0	5.12	28.80	95.0	0.64

[a] C, weight concentration of precursor PEO; T, solvent content in the swollen gel; ex, extractable polymer fraction; Q, volume equilibrium swelling degree; E_G, elastic modulus (dyn/cm²).

Table VI
Influence of the Concentration of PEO Precursor (M_n = 1010) on the Characteristics of the Gels at Equilibrium in Dioxane and in Water[a]

		M_n = 1010			
		dioxane		water	
C, %	% ex	Q	$E_G \times 10^{-5}$	Q	$E_G \times 10^{-5}$
5	no gelification				
7	13	15.54	0.29	6.30	1.81
10	10	18.10	0.88	10.80	0.68
20	2.1	7.59	6.16	5.93	15.8
33	2.4	5.66	17.20	4.35	19.8
50	2.6	4.84	22.00	3.94	24.9

[a] T = 60 °C; E_G in dyn/cm^2.

Table VII
Influence of the Concentration of PEO Precursor (M_n = 1810) on the Characteristics of the Gels at Equilibrium in Dioxane and in Water[a]

		M_n = 1810			
		dioxane		water	
C, %	% ex	Q	$E_G \times 10^{-5}$	Q	$E_G \times 10^{-5}$
5	21	36.76	0.20	30.28	0.24
7	14	25.31	0.72	20.15	0.53
10	1.8	12.50	3.38	10.66	4.25
15	1.0	10.55	7.05	8.55	7.84
20	2.1	8.28		7.16	10.90
33	1.3	7.76	11.6	6.56	12.70
50	0.5	5.28	26.5	4.96	23.30
60	1.3	4.68	32.0	4.53	35.50
bulk	0.3	3.93	45.0	3.86	46.40

[a] T = 60 °C; E_G in dyn/cm^2.

Table VIII
Influence of the Concentration of PEO Precursor (M_n = 5650) on the Characteristics of the Gels at Equilibrium in Dioxane and in Water[a]

		M_n = 5650			
		dioxane		water	
C, %	% ex	Q	$E_G \times 10^{-5}$	Q	$E_G \times 10^{-5}$
20	5.23	23.17	1.01	36.36	0.25
33	2.20	12.84	4.32	15.54	2.15
50	1.82	10.45	6.14	13.26	3.45
60	0.97	7.70	14.20	12.38	6.66
bulk	0.20	4.66	29.60	4.78	37.60

[a] T = 60 °C; E_G in dyn/cm^2.

Three PEO precursors were chosen for these experiments, with M_n = 1010, 1810, and 5650, respectively. Three domains of concentration have to be considered:

Low Concentration ($C \leq 10\%$ by Weight). When the reaction is carried out at low concentration, one can expect an enhanced tendency to cyclization, as suggested by several authors.[39,40,49] This tendency decreases as the molecular weight of the precursor increases. But even after gelification has set in, the amount of extractable polymer is quite high, in agreement with previous observations by Stepto and Waywell.[50] In some cases no gel formation was observed, even after several weeks of reaction.

It should be noted that in the range of concentrations used, all these "nascent" gels are transparent in the dioxane medium in which they were formed. However, they become turbid after extraction and even opaque when they are swollen to equilibrium in water. The effect is more pronounced for gels arising from precursors of lower molecular weight. This indicates that syneresis has taken place during network formation and that the networks formed are macroporous.

Table IX
Influence of the Nature of the Pluriisocyanate on the Characteristics of the Gels at Equilibrium in Dioxane and Water[a]

			dioxane		water	
M_n	type of Desmodur	% ex	Q	$E_G \times 10^{-5}$	Q	$E_G \times 10^{-5}$
1010	N75	2.4	5.66	17.2	4.35	19.8
	L	2.5	5.93	14.3	2.90	24.0
1810	N75	1.3	7.76	11.6	6.56	12.7
	L	2.0	6.29	14.3	4.54	17.3
3400	N75	1.5	13.26	5.07	15.10	2.98
	L	2.0	11.58	5.23	10.10	4.90
5650	N75	2.2	12.84	4.32	15.54	2.15
	L	1.8	15.07	3.34	12.83	2.8
8250	N75	1.2	15.80	3.25	20.33	2.56
	L	2.3	24.45	1.10	33.07	0.68

[a] C = 33%, T = 60 °C; E_G in dyn/cm^2.

These results demonstrate that PEO concentrations of 10% or lower are not appropriate for obtaining transparent homogeneous networks.

Intermediate Concentrations (15% < C < 50% by Weight). For a given PEO precursor, increasing concentrations of the reaction medium will result in decreasing equilibrium swelling degrees (both in dioxane and in water) and in increasing elastic moduli. It should be pointed out also that the higher the concentration, the faster the reaction, as evidenced by the shorter time t_c required to attain gel formation.

All the networks formed in this concentration range are transparent and homogeneous, and they can be considered suitable for biomedical applications. Their hydrophilicity is quite large, and materials with water contents T ranging from 75% to 95% (by weight) have been obtained.

High Concentrations ($C \geq 60\%$ by Weight). Reactions carried out at high concentrations (or in the bulk) yield polymer networks exhibiting high elastic moduli but rather low swelling ratios at equilibrium both in dioxane and in water. The gel point is reached within a few hours of reaction. However, after extraction of the soluble fraction, the gels generally remain opaque, which might be due to partial crystallization of the PEO chains in the networks.

Nature of the Pluriisocyanate. Comparative experiments were carried out with various PEO precursors in dioxane at 60 °C at an overall concentration of 33% by weight, using stoichiometric amounts of either the aliphatic or the aromatic pluriisocyanate (Desmodur N75 or L). The latter compound reacts much faster, and the gel point is reached after 0.5 h instead of 10 h for a PEO precursor of M_n = 1010 and after 3 h instead of 22 h for a PEO of M_n = 8250.

From the characterization data gathered in Table IX it can be concluded that no major difference is observed between the two series of gels swollen in dioxane: the amount extractable polymer being the same, the values of Q and of E_G are nearly the same. However, when swollen in water, gels prepared with the aromatic pluriisocyanate exhibit lower Q values and higher E_G values except for networks with long elastic chains (M_n = 8250). The threshold beyond which water behaves as a better solvent than dioxane is located at M_n > 1810 and $M_n \geq 8250$ for aliphatic and aromatic pluriisocyanate, respectively. This is due to the greater amount of aromatic cross-linker used, as its % NCO is lower than that of the aliphatic one. In addition, all of the networks thus obtained are yellowish, whereas those prepared with the aliphatic Desmodur N75 are colorless.

Table X
Influence of the Polydispersity of the PEO Chains in the Network Exhibiting a Similar Elastic Chain Number-Average Molecular Weight[a]

				dioxane			water		
type of reaction	M_n	polydispersity	% ex	Q	T, %	$E_G \times 10^{-5}$	Q	T, %	$E_G \times 10^{-5}$
single precursor	3400	1.05	2.2	13.26	91.3	5.07	15.1	92.2	2.98
PEO + HMDI + Desmodur N75 (two steps)	3600	1.5	1.3	7.68	85.4	12.0	6.71	82.6	13.1
PEO + HMDI + Desmodur N75 (one step)			0.64	6.81	83.4	15.3	6.09	81.2	15.0

[a] $C = 33\%$, $T = 60$ °C; E_G in dyn/cm^2.

Effect of the Molecular Weight Distribution of the Elastic Chains on the Properties of Hydrogels. All the precursor PEO's that have been used exhibit narrow molecular weight distributions (Table I). It was of interest to establish whether the mechanical properties of the hydrogels formed are influenced by the polydispersity of the elastic chains, and we have investigated this point by carrying out chain extensions prior to cross-linking.

Chain extension reactions provide broader molecular weight distributions, covering a whole range of molecular weights. A precursor PEO of molecular weight 1810 was reacted with hexamethylene diisocyanate (HMDI) as chain extender in dioxane at 60 °C, the molar ratio of [OH] to [NCO] being chosen equal to 2. A kinetic investigation of this reaction will be published elsewhere. Size exclusion chromatography can be used to determine the molecular weight distribution in the resulting polymer.

At the end of this reaction the "chain-extended" PEO has a molecular weight $M_n = 3600$ and a polydispersity index close to 1.5, in agreement with the values expected. This polymer is then further reacted with a stoichiometric amount of the aliphatic pluriisocyanate in dioxane at 60 °C, the concentration being still 33% by weight.

The two reactions (chain extension and cross-linking) can also be carried out in one step, using the same amounts of reactants, the same overall concentration, the same temperature, and a duration sufficient to reach high conversion.

Table X shows the values of the swelling ratios and moduli of the networks obtained by the chain extension method along with the corresponding values measured on networks arising from a single PEO precursor.

It can be observed that networks resulting from one-step and from two-step chain extension processes exhibit almost identical values of Q and of E_G. They swell less and have higher moduli than the networks arising from a single PEO precursor.

This result clearly illustrates the fact that the broadening of the molecular weight distribution (MWD) has a beneficial effect on the mechanical strength of the network with respect to networks prepared from a single PEO precursor with a sharp MWD.

Conclusions

Hydrogels arising from poly(ethylene oxide) precursor chains have been obtained by end-linking using a pluriisocyanate as cross-linking reagent. The reaction was carried out in dioxane solution, using stoichiometric amounts of reagents, under conditions meant to avoid side reactions and to reach high conversion degrees. The amount of extractable polymer was generally low, and, once purified, the networks were characterized by their swelling ratios and their moduli in uniaxial compression, measured in the swollen state.

The parameters influencing the reaction were studied systematically. The molecular weight of the precursor and the overall concentration of the reaction mixture are parameters of great importance, as they determine to a large extent the swellability of the networks to be formed and the moduli they will exhibit. Many of the networks obtained are homogeneous, optically transparent, and sufficiently hydrophilic to be suited for various biomedical applications.

Special attention was devoted to the effect of molecular weight distribution (MWD) of the precursor used, which upon cross-linking, becomes the elastically effective network chains of the hydrogel. It was confirmed that an increase of the breadth of the MWD is beneficial to the mechanical strength of the network. Further work along this line is in progress, and it will be published in the near future.

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Registry No. (PEO)·(Desmodur N75) (copolymer), 88842-45-9; (PEO)·(idealized Desmodur N75) (copolymer), 67554-44-3; (PEO)·(Desmodur L) (copolymer), 58450-59-2; (PEO)·(idealized Desmodur L) (copolymer), 88842-46-0; (PEO)·(HMDI)·(TMP) (polymer), 64422-56-6.

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Kinetics and Thermodynamics of the Metathesis Reaction of Cycloolefins. 2. Molecular Weight Distribution[†,‡]

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ABSTRACT: The metathesis reaction of cycloolefins results in cyclic oligomers and a linear polymer as demonstrated directly by means of GPC in conjunction with a laser small-angle light scattering detector. The polymer shows a most probable molecular weight distribution. The oligomer concentration in the kinetically controlled regime is proportional to $x^{-3/2}$ (x being the degree of polymerization), in accord with a carbene back-biting mechanism. When the thermodynamic equilibrium is established, the oligomer distribution is determined by a ring-chain equilibrium. From a Jacobson-Stockmayer plot of the cyclooctene oligomer concentration a characteristic ratio of 5.8 is derived for polyoctenylene and 13.9 for polynorbornene. In the former case the non-Θ character of the solvent of the reaction, chlorobenzene, becomes evident, yielding a Mark-Houwink exponent $a = 0.68$.

Introduction

The metathesis reaction of olefins is a trans-alkylidenation reaction.[2] The mechanism of the reaction was shown to follow a nonpairwise pathway,[3] and the active species is assumed to comprise a transition-metal-carbene complex,[4] the carbene ligand being exchanged against an alkylidene group of the olefins. The metathesis reaction of cycloolefins[5] results in polymers. According to the carbene mechanism, the polymerization occurs by insertion of the monomer into the transition-metal-carbene bond. The molecular weight of the polymers can be controlled by the addition of acyclic olefins.[6] The polymer is assumed to consist of linear open-chain molecules.[7] In general, besides the polymer, residual monomer[8] and/or a homologous series of cyclic oligomers[9] are formed by a "back-biting" reaction. The relation between acyclic polymer and cyclic oligomers was discussed in terms of a ring-chain equilibrium.[10] The equilibrium, however, is not established instantaneously; in some instances cyclic oligomers are not observed at all. This can be attributed to kinetic hindrance, i.e., to a partially deactivated catalyst.[11] Hence one clearly can distinguish between a kinetically and a thermodynamically controlled regime of the reaction.

The product distribution to be observed under kinetic and thermodynamic control is the subject of the present paper.

Experimental Part

Argon (Linde) was passed over columns filled with molecular sieves, metallic K on Al_2O_3, and Cr(II) on SiO_2 (reduced Phillips catalyst).

Chlorobenzene (Fluka) was purified by chromatography over molecular sieves (4 Å) and aluminum oxide (Woelm, activity super 1) and subsequent refluxing over CaH_2 under an Ar atmosphere; it was distilled off before use.

WCl_6 (Alfa Ventron, "resublimed") was stored under an Ar atmosphere and dissolved in chlorobenzene (0.05 M) before use.

$(CH_3)_4Sn$ (Aldrich) was stored over molecular sieves under an Ar atmosphere. Before use it was dissolved in chlorobenzene (0.1 M).

Cyclooctene (Hüls) was refluxed over K and distilled before use. The absence of cycloocta-1,3-diene was examined by GC. Residual cyclooctane (2-3%) was used as internal standard for the determination of conversion by GC.

Norbornene (Aldrich) was treated in a similar way.

Polymerizations were performed in a glass apparatus under an Ar atmosphere at room temperature. Monomer and solvent (chlorobenzene) were introduced first; the solutions of the catalyst

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[†] Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

[‡] Part 1 is ref 1.

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