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Evaluation of the Length of Primary Chains in Cross-Linked Poly(methacrylate)s

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Two series of cross-linked polymers were examined by equilibrium swelling: poly(methyl methacrylate) cross-linked with different amounts of triethylene glycol dimethacrylate and poly(urethane dimethacrylate)s derived from dicarbamates of oligoethylene glycols monomethacrylates and aromatic diisocyanates. The method of estimation of the length of primary chains has been proposed based on the full form of the Flory-Rehner equation. This required comparing the network parameter values obtained by swelling and those derived from some other sources. In some cases the results had no physical meaning, whereas in others they appeared to be consistent. The latter for poly(urethane dimethacrylate)s yielded the length of poly(methacrylate) primary chains in the range of two to eight, which seemed to be a reasonable result.

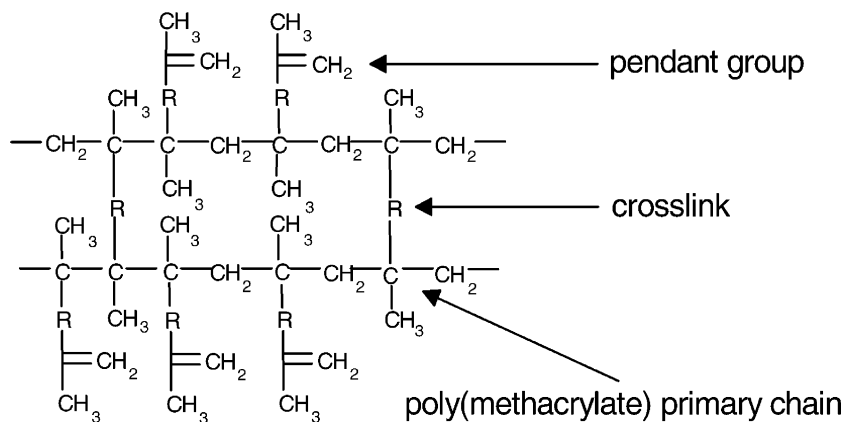
Keywords: Poly(methyl methacrylate-co-triethylene glycol dimethacrylate); Poly(urethane dimethacrylate); Equilibrium swelling; Network parameter; Primary chains

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INTRODUCTION

Cross-linked polymers and network polymers are commonly synonymous terms referring to a considerable fraction of modern polymeric materials^[1a]. However, formally one should distinguish cross-linked polymers as those consisting of relatively long primary chains interconnected with relatively short cross-links, usually differing in chemical structure, whereas in the case of the network polymers primary chains and cross-links are undistinguishable^[1b,2]. The cross-link density (q) in cross-linked polymers used to be defined as molar fraction of chain-repeating units that are cross-linked^[1b]. In polymer networks the number of moles of network chains per volume unit (v_c) is a more adequate measure of cross-link density^[2], where a network chain is that between neighboring branch points. The number average molecular weight of the latter is the so-called network parameter (M_c)^[1a]. Both q and M_c are the basic parameters most frequently determined when characterizing cross-linked systems. Poly(dimethacrylate)s, widely used in dentistry, may be considered cross-linked polymers since they are conceived as to be built of poly(methacrylate) chains cross-linked by monomer molecules that have both double bonds reacted, whereas those with one double bond reacted form pendant groups in the respect to primary chains^[3]. This picture, presented in Scheme 1, is certainly a simplified one since both the polymerization process and the structure of the resulting network are known to be complex ones^[4].

Previously we have reported our attempts to relate the network parameter to the cross-link density and to the conversion of double bonds



SCHEME 1

in the polymers of the series of model urethane-dimethacrylate monomers. Experimental data were based on dynamic mechanical thermal analysis (DMTA) and Fourier transform infrared (FT/IR) spectroscopy^[5]. However, no data have been reported so far concerning the length of poly(methacrylate) primary chains in poly(dimethacrylate)s. Intuitively, we can suspect them to be rather short due to gelation at a very low level of conversion^[4] as well as resulting immobilization, vitrification, and steric isolation^[6]. The question is whether any experimental technique is capable of distinguishing the short poly(methacrylate) chains in the system consisting of cross-links having molecular weights of a few hundreds, pendant groups, loops, entanglements, etc.

Here, we are presenting our proposal of experimental evaluation of the length of primary chains in cross-linked poly(methacrylate)s based on equilibrium swelling. Presuming it to be a difficult task in poly(dimethacrylate)s, in this first approach we have tested a simple, well-defined system based on cross-linked poly(methyl methacrylate) (PMMA) to check whether any reasonable results may be obtained.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, technical grade), triethylene glycol dimethacrylate (TEGDMA, Aldrich), and chloroform (POCh, Gliwice, Poland) were used as received. Benzoyl peroxide (BPO, POCh) was purified by dissolution in chloroform and subsequent precipitation with methyl alcohol.

Polymerization of MMA in Bulk

Molds made of two glass plates, a spacer 2 mm thick, and clamps were filled by use of a syringe with a mixture of MMA and TEGDMA (the cross-linker; 0, 1, 2, 5, 10, and 20 mol%) with 1 wt% of BPO (the initiator) dissolved therein. The molds were placed in a water bath and temperature was raised gradually from 56 to 85°C for 4.5 h. After that, the molds were transferred to a drying oven and the temperature was raised from 85 to 120°C within 18 h.

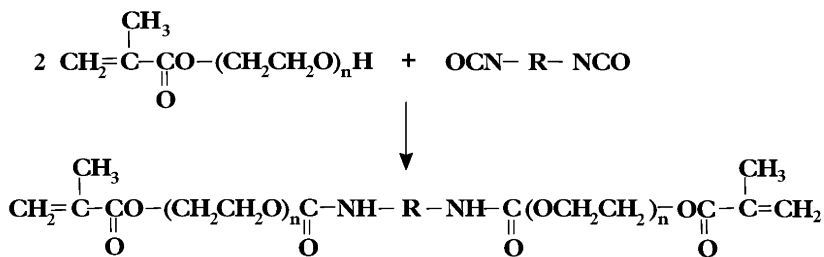
Preparation of Poly(urethane dimethacrylate)s

The urethane dimethacrylates were synthesized from monomethacrylates of oligoethylene glycols having 1 ÷ 4 oxyethylene units (HEMA, DEGMA, TEGMA, and TTEGMA respectively) and

aromatic diisocyanates, 2,4-toluene-diisocyanate (TDI) and 4,4'-methylenebis(phenyl isocyanate) (MDI), as shown in Scheme 2. The monomers were polymerized radically in bulk. The syntheses of the monomers and the polymerization procedure have been detailed in a previous article^[5].

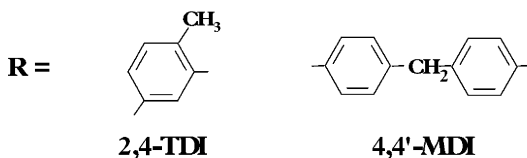
Determination of Equilibrium Swelling by Microscopy

The cross-linked poly(methyl methacrylate)s obtained in bulk and the poly(urethane dimethacrylate)s were subjected to swelling measurements using the method reported by Hill^[2]. A thin strip of the polymer of approximately 0.5 mm edge length was placed onto a Petri dish and covered with a thin glass coverslip. A droplet of chloroform from an eyedropper was contacted with the edge of the coverslip. The solvent was drawn into the narrow gap between glass surfaces and contacted the sample. Swelling was observed by an optical microscope up to a constant increased size that had been reached usually in several minutes and was



OEGMMA:

$n = 1 - 4$ $n = 1$ HEMA
 $n = 2$ DEGMMA
 $n = 3$ TEGMMA
 $n = 4$ TTEGMMA



SCHEME 2

assumed to be in equilibrium. Fractional increase in edge length (l) was calculated according to the following equation^[2].

$$l = \frac{x_2 - x_1}{x_1} \quad (1)$$

where x_1 is edge length of the sample before swelling, and x_2 is edge length of the sample in equilibrium swollen state.

Assuming isometric swelling, the volume fraction of the polymer (ϕ_p) can be expressed as

$$\phi_p = \frac{1}{(1+l)^3} \quad (2)$$

DISCUSSION

Equilibrium swelling is one of the most common methods employed when investigating cross-linked polymeric systems. A classic theory of swelling represented by the Flory-Rehner equation^[1c,7] is a basis of this method:

$$-\left[\ln(1 - \phi_p) + \phi_p + \chi_1 \phi_p^2\right] = (V_1 \rho_p / M_c) \left(1 - \frac{2M_c}{M}\right) \left(\phi_p^{\frac{1}{3}} - \frac{2\phi_p}{f}\right) \quad (3)$$

where M_c is the network parameter, M is the number average molecular weight of primary chains, V_1 is the molar volume of the solvent, ρ_p is the polymer density, f is functionality of branch points, χ_1 is the polymer solvent interaction parameter, and ϕ_p is the volume fraction of the polymer in the swollen gel.

The term $(1 - 2M_c/M)$, the so-called network imperfection factor^[7], usually is omitted by researchers based on an assumption that the system is ideal, hence, M approaches infinity and all the term is reduced to unity. Then, Equation (3) assumes a widely used simplified form^[8]. This enables determination of M_c based on experimental values of ϕ_p . The interaction parameter χ_1 can be calculated for a given structure of a polymer by use of known methods^[9].

Suppose primary chains are short, then $(1 - 2M_c/M)$ is some fractional value. Hence, Equation (3) cannot be used in the simplified form. However, it may be rearranged in the following manner:

$$\frac{M_c}{1 - 2M_c/M} = -V_1 \cdot \rho_p \cdot \frac{\left(\phi_p^{\frac{1}{3}} - \frac{2\phi_p}{f}\right)}{\ln(1 - \phi_p) + \phi_p + \chi_1 \cdot \phi_p^2} \quad (4)$$

The right side of this form is nothing more than a commonly used simplified form of Equation (3). If we denote it as M'_c , following relationship can be derived:

$$M = \frac{2M_c M'_c}{M'_c - M_c} \quad (5)$$

We can now try to use Equation (5) to estimate the length of primary chains, with M'_c assumed to be something like an “apparent” network parameter based on equilibrium swelling, and M_c assumed to be a real network parameter, derived from some other experimental method.

It is evident that if M'_c and M_c tend to be equal, the length of primary chains approaches infinite value and the simplified form of Equation (3) is valid. However, Equation (5) requires $M'_c > M_c$, otherwise there would be no physical meaning. In consequence, the proposed way of estimating M could work if equilibrium swelling yielded higher values of network parameter than did the second method employed. Moreover, since due to experimental errors we never have precise values of both M'_c and M_c , a situation where $M'_c \approx M_c$ would be ambiguous as well.

RESULTS

Pursuing the idea presented in the preceding section we have examined the series of poly(methyl methacrylate)s cross-linked with triethylene glycol dimethacrylate (TEGDMA). The latter monomer has been selected as a cross-linker due to its superior efficiency in cross-linking reactions when compared with the most commonly used cross-linker monoethylene glycol diester^[10]. In Table I we compare swelling results yielding M'_c with calculated, stoichiometry-based values of M_c . Then, the hypothetical length of primary chains, expressed as DP (degree of polymerization) was calculated based on Equation (5). DP was found to decrease smoothly as cross-link density increases. This is quite understandable since cross-linking causes immobilization of growing chains. However, the ratio of M to M_c shows neither tendency remaining in the range of 5.4 to 8.3, suggesting that number of cross-links per primary chain does not depend on cross-link density in this case.

The question is whether the above approach could work as well in the case of poly(dimethacrylate)s, where cross-link density is high, numerous pendant groups act as free ends of chains, entanglements and loops are probably present, and intermolecular non-covalent bonds act as additional branch points. Table II contains the data obtained by equilibrium swelling for the series of poly(urethane dimethacrylate)s compared with the results obtained previously by use of FT IR spectroscopy^[5]. The latter technique yielded direct conversion of double bond (α), which determines cross-link density (q) according to Equation (6)^[11]. The network parameter can be related to q by use of the well-known Equation (7)^[11b]. Previously we have proposed for

TABLE I Experimental data on equilibrium swelling of cross-linked poly(methyl methacrylate)s

mol% of TEGDMA	q	M_c calculated	ρ_p [g/cm ³] ^a	Swelling results				M	$DP = \frac{M}{M^{\prime c}}$	M/M_c
				χ_1^b	ϕ_p	$M^{\prime c}$				
1	0.020	5000	1.17	0.376	0.186	6720	39100	391	7.8	
2	0.040	2500	1.17	0.376	0.235	3947	13600	136	5.4	
5	0.095	1050	1.18	0.377	0.340	1577	6300	63	6.0	
10	0.182	550	1.19	0.377	0.431	827	3300	33	6.0	
20	0.333	300	1.20	0.379	0.551	393	2500	25	8.3	

^aDetermined by a pycnometer.^bPolymer-solvent interaction parameter calculated according to Mikos and Peppas^[9].^cFor calculation of M_c^{\prime} with use of the simplified form of the Flory-Rehner equation; functionality of branch point $f=4$ was assumed.

TABLE II Results of equilibrium swelling and FT IR measurements on poly(urethane dimethacrylate)s

Monomer	MW	ρ_p [g/cm ³] ^a	χ_1^b	ϕ_p	Swelling			M_c from FT IR ^c		
					M_c'			M_c		
					$f = 4$	$f = 3$	$q = \frac{2\alpha-1}{\alpha}$	$M_c = \frac{MW}{q}$	$M_c(f=4) = \frac{MW}{q}$	$M_c(f=3) = \frac{2MW}{3q} - \frac{MW}{3}$
HEMA/ TDI	434	1.43	0.536	0.879	72	52	0.86	505	288	192
DEGMA/ TDI	523	1.48	0.500	0.641	360	289	0.96	545	283	189
TEGMA/ TDI	611	1.45	0.479	0.593	459	375	0.97	630	324	216
TTEGMA/ TDI	699	1.41	0.465	0.574	487	401	0.96	728	379	252
HEMA/ MDI	511	1.41	0.490	0.818	106	79	0.67	763	507	338
DEGMA/ MDI	599	1.53	0.466	0.579	513	422	0.59	1015	716	477
TEGMA/ MDI	687	1.41	0.453	0.551	547	455	0.86	799	455	304
TTEGMA/ MDI	775	1.47	0.443	0.521	675	567	0.92	842	455	303

^aDetermined by a pycnometer.^bCalculated according to Mikos and Peppas^[9].^cBased on the results previously reported^[5].

poly(dimethacrylate)s Equations (8) and (9), which are more adequate in our opinion^[5], where contribution of cross-links in M_c is included, assuming functionality of branch points to be $f = 4$ or $f = 3$, respectively.

$$q = \frac{2\alpha - 1}{\alpha} \quad (6)$$

$$M_c = \frac{MW}{q} \quad (7)$$

$$M_{c(f=4)} = \frac{MW}{q} - \frac{MW}{2} \quad (8)$$

$$M_{c(f=3)} = \frac{2MW}{3q} - \frac{MW}{3} \quad (9)$$

Thus, for each poly(urethane dimethacrylate) we have two possible values of M_c calculated based on swelling experiments with functionality of branch points assumed to be either $f = 3$ or $f = 4$. We could combine both of them with M_c values calculated according to Equation (7). Additionally, M_c for $f = 4$ can be related to M_c from Equation (8) and M_c for $f = 3$ with that from Equation (9). Hence, four pairs of M_c'/M_c could be applied to calculate M using Equation (5).

As is seen from Table II, when taking conversion-based M_c values according to Equation (7), all of them are higher than corresponding M_c' values, hence values of M if calculated by use of Equation (5) would be negative. However, if we assumed M_c to comply with our previous proposal^[5], i.e., Equations (8) and (9), positive values of M (corresponding DP values are given in Table III) have been obtained for most of the

TABLE III Length of primary chains in poly(urethane dimethacrylate)s evaluated by Equation(5)

Monomer	$DP = \frac{M}{MW}$	
	$M_{c(f=4)} = \frac{MW}{q} - \frac{MW}{2}$	$M_{c(f=3)} = \frac{2MW}{3q} - \frac{MW}{3}$
HEMA/TDI	negative	negative
DEGMMA/TDI	5.1	2.1
TEGMMA/TDI	3.6	1.7
TTEGMMA/TDI	4.9	1.9
HEMA/MDI	negative	negative
DEGMMA/MDI	negative	negative
TEGMMA/MDI	7.9	2.7
TTEGMMA/MDI	3.6	1.7

polymers except for poly(HEMA/TDI), poly(HEMA/MDI), and poly(DEGMMA/MDI). Presumably, the latter, derived from the monomers having aromatic cores and short methacryloyloxyethyleneoxy wing groups, have extremely rigid network structure, unable to expand under the action of a solvent. Increase in the number of oxyethylene units to three or four makes the network flexible enough to be swollen and condition $M'_c > M_c$ is attained.

A final result is that comparison of the network parameter values obtained by equilibrium swelling and those derived from conversion measured according to the relationships proposed (Equations (6), (8), and (9))^[5,11] allows estimation of the hypothetical length of primary chains in poly(dimethacrylate)s. Depending on the model assumed, i.e., tetra- or trifunctional branch points, the number average degree of polymerization (DP) amounts to approximately $3 \div 8$ or $2 \div 3$ respectively. The difference seems to be logical since when assuming $f = 3$ the cross-links are treated as independent network chains having $DP = 1$ and thus are thought not to be included in primary chains, whereas when assuming $f = 4$, halves of cross-links participate in neighboring chains^[5]. Nevertheless, in both cases the poly(methacrylate) primary chains thus evaluated seem to be very short, as was supposed.

CONCLUSIONS

Based on the full form of the Flory-Rehner equation it is possible to evaluate the length of primary chains in cross-linked poly(methyl methacrylate). The results have been obtained on bulk polymers where volume fraction of the polymer in the swollen gel was expressed based on fractional increase in edge length of samples and an "apparent" network parameter resulting, was related to the theoretical, i.e., stoichiometry-based one.

When applying this method to poly(urethane dimethacrylate)s the results appeared to have some physical meaning just for less dense networks, i.e., those derived from the monomers having three or four oxyethylene units in wing chains. Moreover, conversion-based network parameter values had to be calculated assuming participation of cross-links. The method yielded the length of primary chains in the range of two to eight methacrylate units. This finding complies with our view on the structure of poly(dimethacrylate)s.

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