

Photocured Polymer Networks Based on Multifunctional β -Ketoesters and Acrylates

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ABSTRACT: The objects of this study are highly crosslinked networks. The base-catalyzed Michael reaction of β -ketoesters with vinyl groups of the pentaerythritol tetraacrylate (PETA) was used for a step grow formation of the crosslinked polymer in dark. The nonreacted vinyl groups and vinyl monomer were built up to the network structure by photopolymerization in the second step of synthesis. An analysis of crosslinked polymers shows that the long spacer between β -ketoester groups in propylenglycol-425-diacetoacetate (PGDAA) favors an extent of reaction compared to pentaerythritol tetrakis (acetoacetate) (PETAA). The excess of vinyl monomers added to polymerization batch functions in the first step of the synthesis as a reactive solvent [triethylene glycol dimethacrylate (TEGDMA); PETA]. The dissolution of reactants has a positive effect on homogeneity, conversion, and crosslink density of prepared networks. The consumption of reactive groups in a course of the network formation, the crosslink density, and dynamic mechanical properties of the prepared networks were determined from Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), sol-gel analysis, dynamic testing, and stress-strain dependencies. The dynamic testing indicates that the networks synthesized in two steps from batches containing an excess of vinyl monomer consist from two highly crosslinked phases interpenetrating each other. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 165–178, 1997

Key words: polymer network; β -ketoester; acrylate; photocuring; properties

INTRODUCTION

The polymer networks with highly crosslinked structures have made these materials suitable to a wide range of applications. The crosslinks fix a geometry of primary macromolecules and provide the specific physical and chemical properties to polymer networks. The search for an optimum topology of macromolecules in order to improve a needed property without significant impairment of other properties of the material still attracts science and practice.^{1,2}

The networks based on vinyl polymers are mostly synthesized from mixtures of mono- and multifunctional monomers by the radical chain crosslinking copolymerization. The mechanism of formation of the polymer networks has an inevitable consequence on network structure, which grows up in an entirely different way from a step-growth mechanism in polycondensation or polymer chains vulcanization. The crosslinked polymer forms very complicated structures of a network that is changing in the course of conversion of the monomers.³

Materials prepared from multifunctional acrylates and methacrylates represent the special group of highly crosslinked polymers useful, for example, for coatings, dentistry, microelectronic,

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and information storage systems.⁴⁻⁷ The description of kinetic features of synthesis of the highly crosslinked dimethacrylates⁸⁻¹² and the modeling a network formation⁸ points out numerous effects that control the network building.

The mechanism of a network building is characterized by various kinds of free radical reactions, which originate macromolecules with pendant vinyl groups and reactive microgel particles. Multifunctional structures in the polymerizing system affected the homogeneity of fabricated article, at least on a submicrometric level.^{3,8,13} The network heterogeneity also arises as a consequence of the inter- and intramolecular cyclization¹⁴ of the growing polymer free radical end.

The steric hindrances gradually reduce reactivity of the dangling double bonds as the extent of reaction increases. Owing to restriction of the polymer segment's mobility in highly cured systems, residual unsaturation is observed as a common phenomenon in rigid vinyl polymers networks.^{15,16} These double bonds are not able react, even in postcuring.³

The significant effect of a nonreacted vinyl groups on the physical and chemical durability of crosslinked polymer^{3,17-19} excites an interest to lower their concentration in cured networks as much as possible. In the fast photopolymerized multiacrylate monomers, the residual unsaturation can be controlled by rate of initiation and length of spacer between vinyl groups.^{15,20,21} The complete double bonds conversion for acrylated poly(tetramethylen ether) macromonomers (250–2000 g/mol M_w) was observed.²²

The further phenomenon observed during the vinyl copolymerization crosslinking is the free radical trapping. The lifetimes of radicals may exceed days or months in dependence on the network crosslinking density.^{13,23,24} These radicals remain trapped and stable in nitrogen, even in the presence of monomer and double bonds dangling on polymer network chains. The long-living free radicals at low conversions accelerate the rate of polymerization (gel effect)¹² and initiate the dark reaction in photopolymerizations after switching off the light.^{21,25,26}

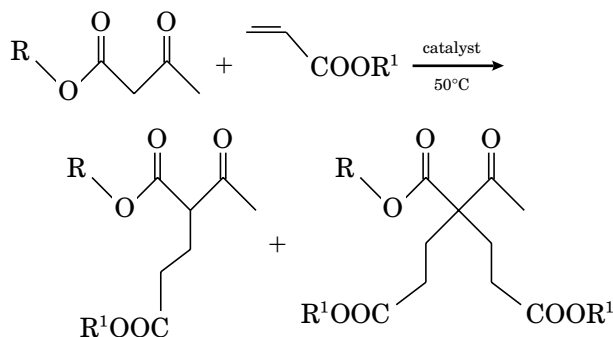
The rate constants of elementary reactions in crosslinking polymerization has been studied intensively.^{8,11,12,14,15,20,21,27} However, the dense network building proceeds scarcely at steady state conditions, and it is inconvenient transfer obtained data from one to another combination of monomers. This difficulty is particularly pro-

nounced in ultrafast photoinitiated curing of multifunctional monomers.²⁸

Less information was published on the physical properties of densely crosslinked networks. Dynamical–mechanical analysis,^{5,29,30} densities of polymer,^{5,7,31} network densities,^{3,22,27} thermal properties,^{16,21,22,27} and surface hardness²² are mostly selected for evaluating the properties of prepared networks.

At present, a satisfactory method does not exist that could enable us to generally predict the relationships between parameters of the copolymerization system and the network structures or network properties. The more complicated the copolymerization systems are, the more we are thrown upon experimental estimation of these correlations.

In this article, we reported the analysis of polymer networks synthesized by Michael reaction of mixtures of various multifunctional acetoacetates and multiacrylates according to Moszner and Rheinberger.³²



The residual double bonds, crosslink density, and dynamic–mechanical properties were determined in the end of the Michael step growth network and in a final product obtained after the second step of a network formation by a photosensitized crosslinked copolymerization.

EXPERIMENTAL

Preparation of Polymer Networks

The five types of crosslinked polymeric systems, based on the following initial reaction mixtures, were studied. The components of batch A are pentaerythritetraacrylate (PETA) and propylene glycol-425-diacetoacetate (PGDAA) in the 1 : 1 molar ratio and the polymerization catalyst DBN in 2 mol %. Batch B contained PETA and PGDAA components in the molar ratio of 3 : 1, DBN cata-

lyst of 2 mol %, and additives of 0.3 wt % of CC and 0.5 wt % of CEMA as sensitizer for the vinyl photopolymerization of nonreacted double bonds and PETA in Michael reaction.

Batch C consisted of components of A [PETA : PGDAA = 1 : 1 with 2 mol % 1,5-diazabicyclo-[4.3.0] non-5-ene (DBN)] to which 40 wt % of triethylene glycol dimethacrylate (TEGDMA) and 0.3 wt % of CC and 0.5 wt % of CEMA was added. The tetraacrylate and tetrakis (acetoacetate) derivatives of pentaerythritol (PETA, PETAA) were used as components for batch 2 (PETA/PETAA = 2) and batch 5 (PETA/PETAA = 5).

Polymerization

The polymer samples of highly crosslinked acrylates were prepared in one step or in two steps if an excess of the comonomer to β -ketoester was used. The polymerization conditions for samples A, B, and C were the same as has been described recently.³² The Michael dark reaction that results for multifunctional acrylates and acetoacetates in a polymer network was started by a DBN catalyst in 2 mol % based on the β -ketoester. Keeping the reaction mixture for 30 min at 20°C, a polymerization was carried out three hours at 50°C in dark. The network formation continued in the second step by a photoinitiated vinyl polymerization of the residual vinyl monomer, and pendant double bonds build up in the primary network in the first step of the synthesis. The reaction was sensitized with camphorquinone (CC) of 0.3 wt % and *N*-(2-cyanoethyl)-*N*-methylaniline (CEMA) of 0.5 wt %. The polymer networks prepared in the dark were irradiated three minutes in the chamber of SPECTRAMAT® (Ivoclar, Liechtenstein) with a visible light of 400 to 500 nm wavelength and an intensity of about 100 mW/cm². The samples containing photosensitizer were protected against an undesirable irradiation by handling under a red light with $\lambda > 600$ nm, far enough from the photoinitiator absorption range. Samples 2 and 5 were polymerized in one step for 72 hours at 60°C.

The samples were prepared in two types of polymerization forms. The block cylinders 30 mm long and 8 mm in diameter were polymerized in nonsealed glass ampoules. The sheets were casted between the glass plates 150 × 100 mm with 0.3 and 0.6 mm Teflon distance foil on the periphery of the forms. The glass plates were coated with a poly(vinyl alcohol) layer of about 0.05 mm thickness.

The provenience of chemicals used in synthesis is as follows: CC, CEMA, and DBN (Aldrich, Germany); PETA (Sartomer, Pennsylvania); TEGDMA (Esschem, Pennsylvania); and PETAA and PGDAA were synthesized by acetoacetylation of the corresponding hydroxy compound with 2,2,6-trimethyl-4H-1,3-dioxin-4-one (Aldrich, Germany) according to Clemens and Hyatt.³³ All the commercial chemicals used, as well as synthesized monomers and additives, were of at least 95% purity.

Crosslink Density

The crosslink densities of the prepared polymer networks were determined in three ways. The first is by the application of the Flory–Rehner equation that relates polymer network swelling behavior to molecular weight between crosslinks M_c and the polymer–solvent interaction parameter χ , as follows³⁴:

$$\frac{1}{M_c} = -\frac{\ln(1 - v_p) + v_p + \chi v_p}{\rho V_s (v_p^{1/3} - 2v_p/f)} \quad (1)$$

Here ρ is the polymer density, v_p is the polymer volume fraction in a solvent saturated network, and V_s is the molar volume of solvent. The functionality of crosslinking agent is usually assumed to be 4. Swelling in acetone, chloroform, and toluene at 25°C were performed to equilibrium with the changing of the pure solvent three times. The interaction parameter χ was calculated using the equation and values of solubility parameters δ_p and δ_s of polymer and solvents, which are presented in the literature.^{35,36}

$$\chi = \chi_{\Delta S} + V_s (\delta_p - \delta_s)^2 / RT \quad (2)$$

$\chi_{\Delta S}$ is the entropy term and the value 0.34, which is valid for most nonpolar systems was used.^{35,36} The following values for δ [cal/cm²]^{1/2} were applied in calculation χ , as follows: $\delta_p = 9.4$ and $\delta_s = 10$; with 8.9; 9.3 for acetone, toluene, and chloroform.

The values of χ calculated for acrylate polymers and solvents used in this work were 0.385; 0.385 and 0.450 for swelling in acetone, toluene, and chloroform, respectively. The specific densities ρ of polymer networks were determined by weighing the samples in the pycnometer.

Network:	A	B _I	B _{II}	C _I	C _{II}	2	5
ρ [g/cm ³]:	1.19	1.18	1.21	1.18	1.25	1.23	1.26

The two other methods of the M_c determination are based on measuring mechanical properties of networks. The mechanically effective M'_c was calculated from the tensile storage modulus measured in dependence on temperature. Tensile polymer properties were determined on Rheovibron viscoelastometer (Toyo Baldwin Co. Ltd., Japan). Most of the dynamic measurements were performed from -60 to $+120^\circ\text{C}$ with frequencies of 11 and 110 [rad/s]. The heating rate of the sample $2^\circ\text{C}/\text{min}$ and the sample sizes of 35 mm length, 5 mm width, and 0.3 or 0.5 mm thickness were used.

The Analysis of Residual Double Bonds

The Nicolet Impact 400 FTIR spectrometer was used to record the spectra of the polymer dispersed in KBr pellet. The standard baseline technique was used for evaluating spectra.³⁷ The infrared (IR) spectrum for the monomer mixture of PETA and PETAA in molar ratio 2 : 1 is shown in Figure 1. The sharp absorption band at 810 cm^{-1} ($=\text{CH}_2$ twisting) belongs to acrylic ester monomers. The absorption coefficient $2\,940\text{ (cm}^2/\text{g)}$ was determined and used in calculations of nonreacted acrylate double bonds concentration in examined networks. The small twin peaks at 1639 and 1620 cm^{-1} ($=\text{CH}_2$ stretching) are relevant to vinyl double bonds, however, with the substantially lower absorption coefficients.¹⁵ The extent of carbonyl groups of β -ketoester PETAA (resp. PGDAA) conversion was estimated from absorption band at 1360 cm^{-1} [absorption coefficient $303\text{ (cm}^2/\text{g)}$], which is absent in the spectra of vinyl monomers and changes during the reaction. The intense absorption bands at 1718 and 1745 cm^{-1} (associated with the $\text{C}=\text{O}$) are shielded with $\text{C}=\text{O}$ groups of vinyl ester monomer (band at 1725 cm^{-1}) and fuse to one broad peak unsuitable for an analysis. The methacrylate monomer PEGDMA concentration was determined from the absorption band at 946 cm^{-1} , characteristic for methacrylate $=\text{CH}_2$. The estimated absorption coefficient used for determination of remaining PEGDMA unsaturation was $1700\text{ (cm}^2/\text{g)}$.

DSC was applied as an alternative technique for determination of the accessible residual double bonds by monitoring the heat release during heating a sample to elevated temperatures. A Perkin-Elmer DSC-2 apparatus was used. The instrument was calibrated using indium.

RESULTS AND DISCUSSION

A wide variety of applications of the highly crosslinked polymers are based on building up the network from low molecular multifunctional compounds. An advantage of low viscosity of starting polymerization batch is, however, combined with special features of the reaction kinetics, which have not been characterized well. Multifunctional monomers, in contrary to simple reactants, show an anomalous behavior in the polymerization in the highly crosslinked medium.³

The object of this study is evaluation of the properties of highly crosslinked networks with predominant acrylic crosslinks. The selection of components and their concentrations for studied polymerization systems are based on recent results³² obtained in the study of step growth formation of polymers by a Michael reaction combined with vinyl polymerization. Three-dimensional networks prepared in this way arise transparent, from soft, nonelastic to hard, brittle crosslinked materials. The required hardness and strength of these polymers increases when the molar ratio of vinyl groups to keto groups increases too. The functionalities of a monomer higher than two, attached with a short spacer to a small molecule also favors the polymer network hardness. So the crosslinked polymers used in this study were prepared from polymerization batches with an excess of vinyl double bonds over the concentration of β -ketoester groups. The excess of vinyl monomer over the β -ketoester is necessary to ensure a sufficient extent of Michael reaction before the gel point is attained. From this moment, the mobility of the reacting molecules progressively decreases to the extent that crosslinking ceases. Tables I and II present the portions of the functional groups that remains unreacted in the prepared

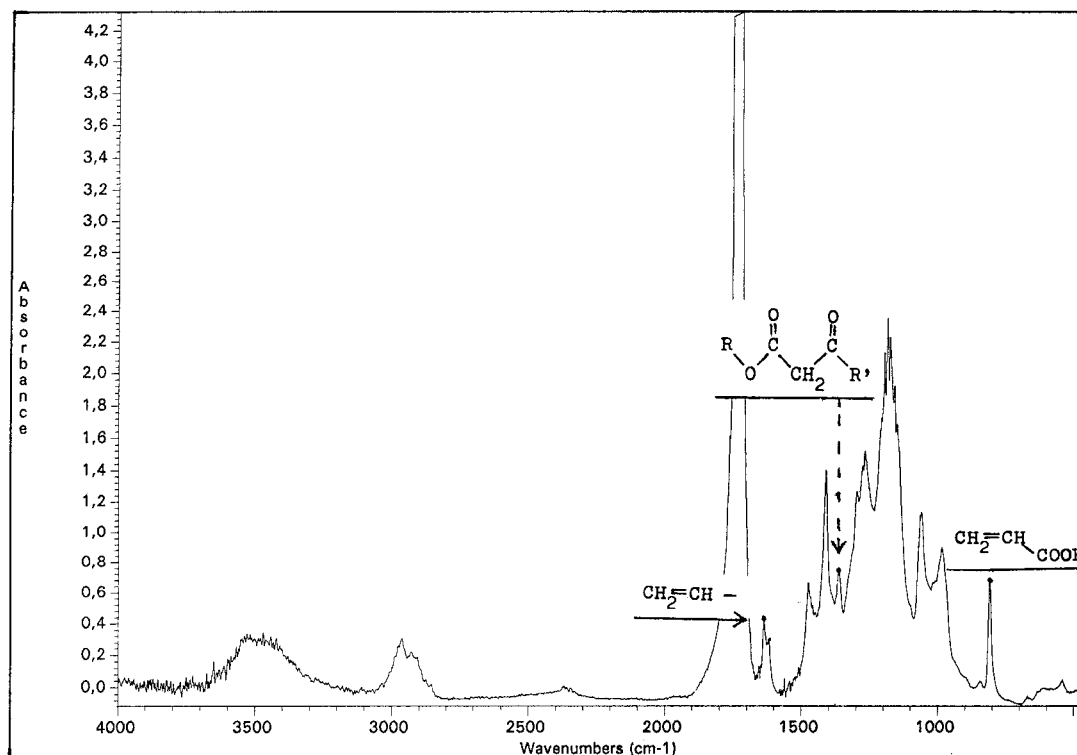


Figure 1 The IR spectrum for monomer mixture of PETA-PETAA in the molar ratio of 2 : 1. The diminishing of absorption bands at 810 and 1360 cm^{-1} resp. follows the extent of PETA and PETAA conversion.

polymer networks A, B, C, 2, and 5 at the end of the Michael reaction (dark reaction) and after the crosslinking photopolymerization of a further portion of the remaining monomer and the residual dangling vinyl groups.

The acrylate monomer is consumed by the Michael reaction and by free radical polymerization. In the first stage of a network formation in dark, an extent of the free radical chain reaction is low. A thermal polymerization of acrylate monomers at 50°C is insignificant in the absence of an initiator. As can be seen from an analysis of samples 2 and 5, the combination of PETA with PETAA, the acrylic and β -ketoester derivatives of pentaerythritol, polymerize to networks with considerably high residual acrylic and β -ketoester functions, even after heating the polymer to 200°C for 30 min. The polymerization of PETAA with a high excess of PETA at 60°C consumes about one-third or one-fifth of vinyl groups.

The thermal treatment of the network to higher temperatures releases the initially hindered polymer segments for further crosslinking reactions.^{3,15,25} An amount of approximately 90 resp. 84% of acrylic and 48 resp. 57% of β -ketoester

groups can be finally converted to crosslinks in networks 2 and 5. The thermal curing favors the acrylate groups' free radical copolymerization rather than the Michael reaction with β -ketoester. This can be deduced from a higher increase of conversion of vinyl double bonds compared to β -ketoester groups: 2.7 to 1.3 times for sample 2; resp. 4 to 2.5 times for sample 5.

The unreacted vinyl groups that remain in the cured polymer can undesirably affect the long-term properties of the crosslinked material. The network with a higher extent of reaction was synthesized from the PETA monomer bearing a high density of polymerizable functions in combination with the PGDAA component that β -ketoester groups are separated with a long spacer. (Table I, sample A). Combination of these monomers facilitates the crosslinking to a rarely reached extent of reaction in the highly crosslinked networks. The effect of the chain length between reactive vinyl groups on an increase of their conversion was also observed for series of poly(ethylenglycol diacrylates)²¹ and poly(tetramethylene ether) glycol diacrylates oligomers.²²

Sample A, which represents the network,

Table I The Residual Nonreacted Functional Groups in the Synthesized Networks: FTIR Analysis; Polymerization Batches 2, 5, A, and B

Sample ^a	Components in Batch		PETA wt % (A ₈₁₀ cm ⁻¹ ; acrylic C=C)	β -Ketoester (A ₁₃₆₀ cm ⁻¹ ; wt %)
	Monomers	Initiator		
2	PETA : PETAA	DBN	66.3	63.2
2 ₂₀₀	2 : 1		9.9	52.1
5	PETA : PETAA	DBN	78.0	76.8
5 ₂₀₀	5 : 1		15.6	42.6
A _I			11.3	12.1
A _I ^b	PETA : PGDAA	DBN	5.2	6.2
A _I ^c	1 : 1		4.5	4.0
A ₂₀₀			3.2	5.0
B _I ^d			39.7	21.9
B _I	PETA : PGDAA	DBN	27.3	20.0
B _{II}	3 : 1	CC	20.1	20.1
B _{II200}		+ CEMA	13.6	19.8

^a Index 200 means the sample was additionally cured at 200°C/30 min; index I means the sample was polymerized in dark at 50°C/3 h; index II means sample I was photocured in the second step; Samples 2 and 5 were polymerized in dark at 60°C/72 h.

^b Value determined 1 month later.

^c Value determined 9 months later.

^d B_I^d, system without photosensitizer.

builds up predominantly by the Michael reaction, in the IR spectroscopic analysis, based on the twisting vibration of the acrylic double bond at 810 cm⁻¹, and the absorption band at 1360 cm⁻¹ show that more than 90% of acrylate vinyl groups and β -ketoester groups were consumed during the synthesis. The IR absorption at 1639 cm⁻¹, which is also relevant to vinyl double bonds, shows a substantially lower conversion for sample A. This is, however, the absorption region where the KBr impurities may interfere with IR determination of vinyl groups. Moreover, the absorption coefficient at 810 cm⁻¹ exceeds 2.6 times this value at

1639 cm⁻¹ and favors the measurements at 810 cm⁻¹.

The sol-gel analysis shows that the 91.8 wt % of the sample A is insoluble in chloroform and contains 6.6% nonreacted acrylic functions based on PETA in the batch. So we can anticipate that residual acrylate functions are bonded to the network structure as dangling vinyl groups. The reaction proceeds further at room temperature up to 95% conversion of PETA; nevertheless, a complete conversion was not achieved either by post curing at 200°C.

The heterogeneity of the highly crosslinked

Table II The Residual Nonreacted Functional Groups in the Synthesized Networks C: FTIR Analysis

Sample ^a	Components in Batch		PETA wt % (A ₈₁₀ cm ⁻¹ ; acrylic C=C)	β -Ketoester (A ₁₃₆₀ cm ⁻¹ ; wt %)	TEGDMA wt % (A ₉₄₆ cm ⁻¹ ; methacrylic C=C)
	Monomers	Initiator			
C _I ^b	PETA : PGDAA		15.8	24.3	83.6
C _I	1 : 1	DBN	15.0	25.8	31.9
C _{II}	+ TEGDMA 40 wt %	CC	4.9	21.2	16.7
C _{II200}		+ CEMA	1.1	21.3	8.8

^a Index 200 means the sample was additionally cured at 200°C/30 min; index I means the sample was polymerized in dark at 50°C/3 h; index II means sample I was photocured in the second step.

^b C_I^b, system without photosensitizer.

networks prepared by polymerization of multifunctional monomers can be diminished in systems with low viscosity.^{3,18,28} The diluent enhances the diffusion of reactive groups that leads to a more uniform course of the polymerization and a higher degree of monomer conversion and crosslink density. The positive effect on forming homogeneous material also has better mixing of polymerization batch components. However, the physical-mechanical properties can be maintained, and even improved, if the reactive solvent is used and converted to polymer in second step of synthesis. This is the case of polymerization systems B and C (Table I). The vinyl monomer added in excess functioned in the dark Michael reaction not only as a reactant but also as a diluent, which is photopolymerized in the second stage of forming a crosslinked material. The additional crosslinks in the Michael network are built up and the acrylate resp. methacrylate (sample C) network interpenetrates the primary PETA-PGDAA crosslinked polymer structure. This photocuring increases the extent of crosslinking and improves a mechanical strength of the primary soft Michael polymer network. The conversions of polymerizable groups presented for B and C samples in Tables I and II show that all accessible β -ketoester groups join in the network with about a 80 resp. 75 wt % extent already at the first stage of reaction. The vinyl groups, however, are consumed step by step.

The 60% PETA vinyl groups were converted by the Michael reaction to crosslinks in the polymerization system consisting from monomers and DBN. The polymerization batch that was completed with the photoinitiator polymerized in dark (Michael reaction) to the higher vinyl groups conversion of about 73 and 85% for the B_I resp. C_I polymer.

A photopolymerization in the second stage of network synthesis rapidly converted the soft network to hard material with 20% resp. 5% residual acrylic groups. This is almost the maximum conversion of the accessible bonds by a crosslinking polymerization. The additional 6 and 4% resp. of vinyl groups can be reacted and built up in the network by the polymer curing thermally to 200°C for 30 minutes.

Still, polymer network C, which was also formed by TEGDMA, shows the IR intensities of the C=C absorbance peak at 946 cm⁻¹ considerably high. This observation agrees well with known low reactivity of methacrylates compared to acrylates in the Michael reaction.³⁹ The poly-

mer network from the monomers composition C is formed in dark predominantly by the Michael reaction of PGDAA with PETA. Nevertheless, the thermal vinyl polymerization at 50°C in dark proceeds in C_I slowly to 14% methacrylate monomer conversion after 3 h. The conversion of TEGDMA at the end of a dark reaction was 68% in the system C_I, which contains also the photoinitiator. The TEGDMA fast polymerization in the second stage was initiated by light, to 83% conversion (Table II, sample C_{II}).

The data in Table I and II completed with sol-gel analysis (Table IV) leads to a conclusion that a part of the unreacted double bonds is incorporated to the network structure as the dangling vinyl group. This is associated with a different reactivity of the monomer functional groups and those that are bounded to macromolecular chains through the multifunctional monomer links.^{3,14,40,41} The decrease of reactivity of a pendant vinyl groups is referred in the methyl methacrylate with 15 mol % ethylene glycol dimethacrylate copolymerization to be approximately of two decimal orders lower than that of the monomer.⁴⁰ Thus, all highly reactive multifunctional monomers used in this study are, above all, built up to the network polymer chains by one reactive group. The low conversion of double bonds, in average, one reacted per monomer at maximum conversion, was also found for radical photopolymerization of multifunctional acrylates with high density of vinyl unsaturation.¹¹ It should be mentioned that the presented systems (A, B, C, 2, and 5) were crosslinked predominantly by addition of acrylate monomer to β -ketoester molecules. Vinyl polymerization is slow during the dark Michael reaction in the first step of building up the network. Nevertheless, the similar low average conversion was observed for reactive groups in PETA and PETAA monomer molecules. An increase of the share of reacted vinyl groups per monomer molecule was achieved by changing PGDAA for PETAA (samples A, B, and C) and by enriching the C batch with an additional component, TEGDMA. The higher extent of reacted functional groups per monomer agree with findings that a longer spacer between two reactive groups facilitates polymerization of dangling double bonds^{21,22,27} due to their higher diffusibility.

Based on this mechanism of network growth, a substantial increase of strength and hardness of networks during the photocuring stage of reaction is understandable, and even an amount of

Table III The Exothermic Heat of Analyzed Networks by DSC Calorimetry

Sample No.	Time after Preparation (weeks)	ΔH (cal/g)	$T_{p_{max}}$ (°C)	Weight Percent of Monomer Reacted During DSC Scan	
				From ΔH	From FTIR ^a
2	0	67.2		74	56
2	2	30.4	122	34	—
2	6	19.4		21	—
5	0	90.7		82	62
5	2	47.1	127	42	—
5	6	30.4		27	—
A	—	12.7	359	22	8
B _I	—	26.2	126	26	14
B _{II}	—	0	—	0	—
C _I	—	19.3	113	31	37
C _{II}	—	0	—	0	—

Temperature scan 10°C/min. Polymer samples after the dark reaction.

^a Conversion calculated from FTIR analysis of networks after the dark reaction and after curing to 200°C in air.

the consumed double bonds was small compared to the first stage of polymerization (Table II).

The combinations of multifunctional monomers used in this study are photopolymerized rapidly at room temperature to the hard and glassy acrylate networks. The reaction proceeds below the glass transition temperature of synthesized polymer. The high crosslink density of these networks provides not only dimensional stability but also hinders translation and segmental diffusion and limits functional groups conversion. The higher extent of polymerization can be achieved by an increase of temperature since favoring the motion of the polymer segments and the constrained dangling vinyls.²⁵

The temperature scan during the DSC calorimetric measurement of the networks prepared by crosslinking polymerization is a useful additional technique to the IR spectroscopy of polymer networks analysis. The exothermic heats of reaction arising from the polymerization of a residual acrylate and methacrylate monomers and pendant functional groups after the dark reaction are presented in Table III. The second thermal scan over the same temperature range did not show any further thermal process in the sample. This result demonstrates that curing by heat significantly reduced the residual monomer in the highly crosslinked polymer. The slow polymerization of vinyl groups at room temperature in synthesized networks supports also a decrease of an exotherm in DSC measurements after 2 and 6 weeks in samples 2 and 5 (Table III). The heat release dimin-

ished to about one-third of that amount determined immediately after Michael network synthesis. The extent of vinyl groups polymerization calculated from ΔH , however, shows substantially higher conversions compared to values based on FTIR analysis. Since no special arrangement for oxygen elimination from DSC pans was made, the observed difference probably arises from oxidative reactions, which proceed parallel to polymerization.

The photocuring of the Michael networks synthesized from the batches with an excess of vinyl monomer to β -ketoester has a similar effect on the extent of the crosslinking reaction as thermal curing. The networks after photocuring in the second step of the synthesis did not release heat already at the first temperature scan up to 360°C. It can therefore be concluded that the absorbed radiation energy by photoinitiator molecules generates not only initiating species, but, through the various nonradiative deactivation pathways, increases also the local temperature and segmental motion. So the higher extent of reaction compared to thermal polymerization can be reached by photocuring at substantially lower surrounding temperatures (Table III).

Network Density

The swelling of polymer networks in solvents for the same uncrosslinked polymers provides data suitable to characterize network structure, as follows: (1) the amount of polymer that is not incor-

Table IV The Sol–Gel Analysis of the Synthesized Polymer Networks

Sample	Acetone Gel (wt %)	Swelling Ratio	Toluene Gel (wt %)	Swelling Ratio	Chloroform Gel (wt %)	Swelling Ratio
2	88.5	1.9	89.7	1.2	87.6	10.5
5	74.7	2.0	79.1	1.4	73.7	14.0
A	93.9	1.8	93.5	2.2	91.8	4.4
B _I '	62.8	3.6	59.1	3.3	49.9	10.9
B _I	68.8	2.9	81.3	3.5	81.0	9.0
B _{II}	99.5	1.3	98.8	1.5	97.6	1.5
C _I '	61.0	2.0	61.7	3.2	59.3	6.4
C _I	81.3	2.1	86.0	2.5	—	—
C _{II}	87.7	1.6	87.7	1.9	84.0	3.3

Samples were swollen in acetone, toluene, and chloroform to equilibrium at 23°C.

porated into the network structure (sol fraction), and (2) the swelling ratio of insoluble polymer (gel fraction). Swelling ratio is related to the crosslink density and M_c , the number-average molecular weight between crosslinks, which is the important structural parameter of the polymer network. The magnitude of M_c has a significant effect on the properties of crosslinked polymer, and its determination has a principal importance in the network characterization. The volume fraction of the polymer in the swollen gel determined from equilibrium swelling in acetone, toluene, and chloroform (Table IV); the calculated χ ; and determined densities of synthesized polymers were used for calculation M_c according to eq. (1) developed by Flory–Rehner.³⁴ (Table V) Unknown values of χ were estimated using eq. (2) and parameters of solubility from the literature.^{35,36} For ace-

tone, toluene, and chloroform, χ values used were 0.385, 0.385, and 0.450, respectively.

The sol–gel analysis of final networks have shown that their complete insolubility set in all thermal postcured samples at 200°C/30 min. The nearly full insolubility, very close to 99%, was found for the photocured network B, which is composed of PGDAA and an excess of PETA. The substantial difference between these two thermal and photocured crosslinked polymers is in the density of the network. The swelling ratio of the crosslinked polymer B_{II} is 1.4; but after additional thermal curing at 200°C/30 min, the sample B_{II200} does not swell at all. All polymer networks studied in this work after high-temperature curing behave in the same way. An absence of swelling in highly crosslinked samples makes this method impracticable for determination of M_c . An amount of polymer that is not incorporated into the network structure (sol fraction) set up the synthesized polymer samples in the following order. Sample B_{II} was prepared from PETA : PGDAA = 3 : 1 (sol 1.4%). Sample A was composed of PETA : PGDAA = 1 : 1 (sol 7 wt %). Sample 2 was composed of a copolymer from PETA : PETAA = 2 : 1 (sol 11.4 wt %). Sample C_{II} was prepared with 40 wt % TEGDMA (sol 13.5 wt %). Sample 5 was composed of PETA : PETAA = 5 : 1 (sol 24.2 wt %).

Presented values are an average of soluble fraction found in swelling the networks in acetone, toluene, and chloroform. It should be noticed that the amount of gel is independent of the type of solvent used for extraction. The determined values are very close each to other. The swelling ratio depends, however, on the quality of solvent considerably (Table IV). Disregarding the fact that

Table V Length of the Polymer Chain Segments M_c Calculated from Sol–Gel Analysis of Synthesized Networks

Sample	M_c (g/mol)		
	Acetone	Toluene	Chloroform
2	850	140	—
5	1230	320	—
A	770	1650	3260
B _I '	5110	6660	22050
B _I	2960	4320	15330
B _{II}	140	400	180
C _I '	940	4530	7490
C _I	1150	2330	2830
C _{II}	500	1100	1810

Gel swelled to equilibrium in acetone, toluene, and chloroform at 23°C.

the composition of sol fractions was not analyzed for the presence of the monomer, an increase of spacer length between functional groups has a positive effect on the intermolecular crosslinks formation. However, the large excess of the vinyl monomer over the β -ketoester in networks C and 5 increases the sol fraction, probably through an intramolecular cyclization and formation of soluble submicrometric gel particles.

In the two-step growth networks with an excess of vinyl monomer (samples B_I and C_I), the photoinitiator CC-CEMA (quinone/amine couple), even in dark, initiates the radical polymerization. This can be seen from FTIR analysis (Tables I and II) and results from swelling experiments by comparing the data for B_I, C_I and B_I['], C_I['] without a photoinitiator (Table IV). The extent of consumed vinyl groups and an amount of the soluble part of the sample pointed out that during the dark period of building the network B_I, C_I, the vinyl polymerization also proceeds. The Michael network prevails, however, over the vinyl network that interpenetrates the first one. The existence of two phases in samples B_{II} and C_{II} supports the dynamic mechanical behavior of photo- and thermal-cured polymer networks. The variation of storage modulus E' and loss factor $t_g \delta$ as a function of temperature shows the two glass transition areas. The T_g for sample B_{II} is 25 and 70°C; for samples C_{II}, T_g is equal to 25 and 75°C (Table VI; Figs. 3 and 5).

The M_c is more instructive characteristic that reflects the density of prepared networks. The calculated values are shown in Table V. The crosslink density in the Michael networks varies with the length of spacer between reactive groups in the monomer molecules. A withdrawal of active parts in the multifunctional monomer favors the accessibility of the remaining polymerization functions already built up in the network structure. A change of PGDAA for PETAA decreases the average network density in the system with PETA of approximately of one decimal order. The extent of reaction, however, is substantially higher for the PGDAA-PETA batch.

A dilution of the polymerization system with a reactive solvent, for example, with an excess of acrylate to β -ketoester (sample B) or methacrylate (sample C), increases the chain mobility and β -ketoester conversion. The density of crosslinks in the Michael networks prepared in this way are lower than in networks from equimolar monomer composition. The M_c based on the swelling net-

works in toluene are B_I['] = 6660 [g/mol] and C_I['] = 4530 [g/mol]. A more dense, but still soft Michael network forms the system also containing a photoinitiator. The M_c calculated for B_I = 4320 [g/mol] and for C_I = 2330 [g/mol].

The networks synthesized in the presence of diluent have specific properties compared to non-diluted systems.³ One of the interesting differences that can be expected is so-called inverse syneresis.⁴² In the system where the diluent for the formed polymer is the monomer, the uptake of the monomer by the network structure causes its volume expansion. The crosslinked polymers of compositions B and C after the first step of synthesis are soft and rubbery materials with a bulk density of 1.18 g/cm³. These are converted to highly crosslinked brittle polymer networks only after additional photocuring or thermal curing. The M_c values for fully cured final networks are close to each other for all prepared polymers. The material density 1.21 resp. 1.25 g/cm³ indicates that the primary structure was not fixed and that the second step of network building caused its shrinkage.

Dynamic Mechanical Analysis of Networks

The dynamic behavior of crosslinked polymers can be used as useful additional information about the network topology. The mechanical damping is a convenient method for a determination of the T_g of the glass transition and the degree of crosslinking.^{30,43} The dynamic analysis has been used also in characterization of the phase relationships in the multicomponent polymer systems.⁴⁴

The development of a crosslinked structure of the two-step buildup network is illustrated by the dynamic mechanical spectra in Figures 2–5. The polymerization of composition C (PETA-PGDAA-TEGDMA) seems to be instructive for the description of the network properties after the single steps of a synthesis. Figure 2 shows the course of the storage modulus E' for two Michael networks with the same starting monomer composition, but alternatively with and without the photoinitiator for second step polymerization (C_I resp. C_I[']). The two further spectra belongs to a photocured network (C_{II}) and an additional thermal treated network (C_{II200}). The dependencies of loss factor $t_g \delta$ and the loss modulus E'' on temperature are presented in Figures 3 and 4.

The spectrum of E' (Fig. 2) contains important

Table VI The Mechanical Effective M'_c (g/mol) Calculated from the Dynamic-Mechanical Characteristics of Synthesized Polymer Networks According to the Relation $M'_c = 3\rho RT(1-2f)/E'_N$

Sample	T_g (°C)		Log E'_N (Pa)		M'_c (g/mol)	
	11 Hz	110 Hz	11 Hz	110 Hz	11 Hz	110 Hz
2	26	32	8.18	8.28	33.1	26.8
2 ₂₀₀	—	80	—	9.77	—	1.0
5	18	25	7.91	7.95	63.2	58.0
5 ₂₀₀	—	40	—	9.45	—	2.0
A _I	10	15	8.13	8.17	34.5	33.7
A _{I200}	26	40	8.17	8.25	34.7	30.0
B _I	2	5	7.40	7.50	178.0	143.0
B _{II} ^a	20	25	9.28	9.40	2.6	2.0
	60	70	9.06	9.16	4.8	3.9
C _I '	-12	-5	7.88	7.92	61.2	52.7
C _I	5	12	8.44	8.52	16.5	14.0
C _{II} ^a	15	25	9.12	9.22	6.2	5.9
	65	75	8.90	8.94	4.3	4.2
C _{II200}	48	105	7.23	7.18	320.0	421.0

Storage modulus E'_N is defined as E' measured at 30°C above T_g . T_g of polymer samples is referred as a temperature of the maximum value of $t_g \delta$.

^a The temperature of the second peak (T_g) on the $t_g \delta$ versus temperature curve.

structural information of crosslinked polymers. The theory of rubber elasticity^{2,34} relates the M_c to the plateau of elastic modulus (E'_N) at tem-

peratures well above T_g according to $M'_c = 3\rho RT(1-2f)/E'_N$, where ρ is the density of polymer, R is the gas constant, T is temperature

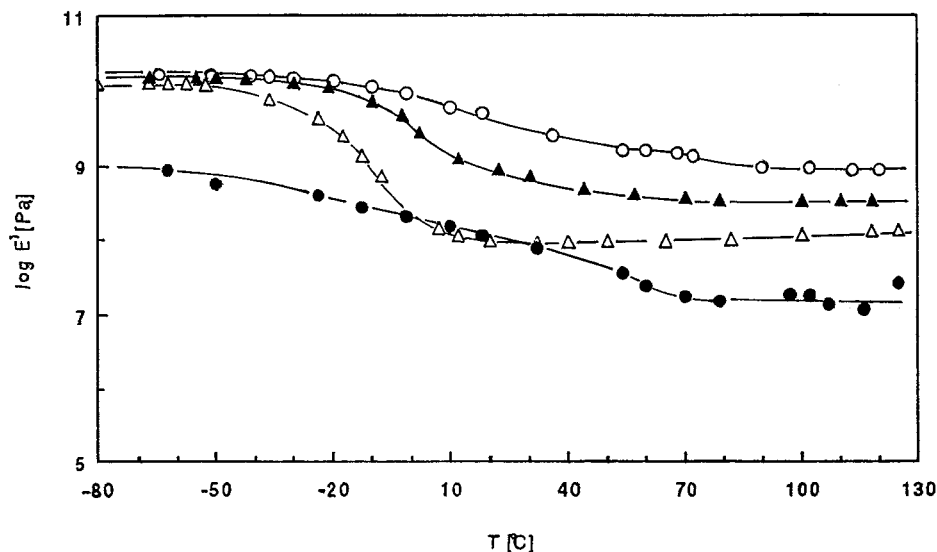


Figure 2 The storage modulus E' in dependence on temperature in the dynamic testing (110 Hz). Crosslinked polymer samples of PETA-PGDAA (1 : 1) + 40 w % TEGDMA. C_I': The first step of synthesis; dark reaction; initiator DBN 2 mol %; without photoinitiator (Δ). C_I: The first step of synthesis; dark reaction; initiator DBN 2 mol %; photoinitiator for the second step of synthesis was added (\blacktriangle). C_{II}: Polymer network obtained in the second step of reaction, photocuring (\circ). C_{II200}: Additional curing of C_{II} at 200°C/30 min (\bullet).

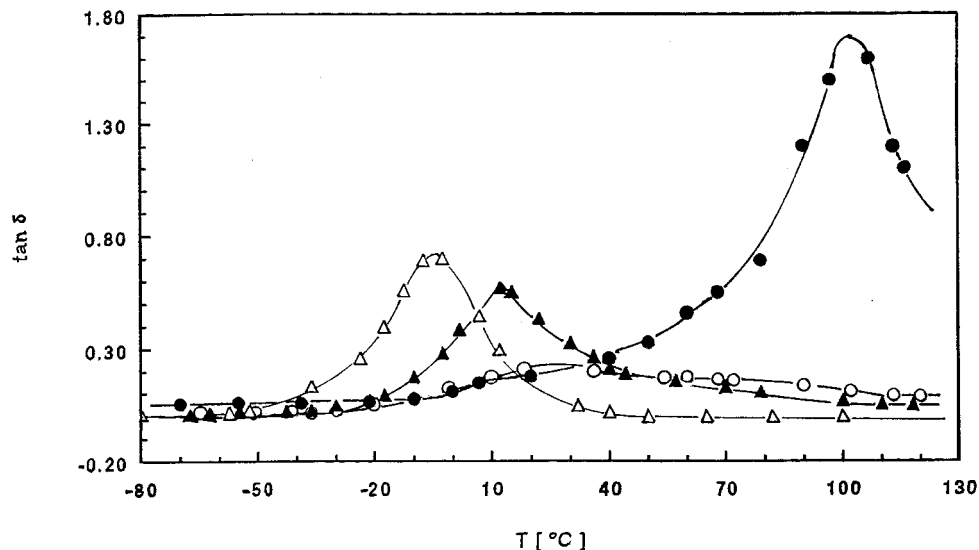


Figure 3 The loss factor $t_g \delta$ in dependence on temperature for the same crosslinked polymers as in Figure 2.

in K, and f is the functionality of a crosslinker. The calculated values of M'_c are presented in Table VI.

The values of M'_c deduced from E' show a crosslink density of about one to two decimal orders higher in comparison with data obtained from swelling and stress-strain measurements. The equation used for calculation M'_c certainly does not hold fully for highly crosslinked networks used in the present study. The relaxation times

of the polymers are longer than period of oscillation, and the E' in rubber state is not independent of the angular frequency. So the Young's moduli derived from dynamic tests for lack of relaxation² and network imperfection⁴⁵ are often higher than the results from static measurements. Moreover, the tested networks, namely, composition C, can consist of two networks embedded each to other with the complicated topology. These crosslinked polymers are expected to exhibit higher moduli in

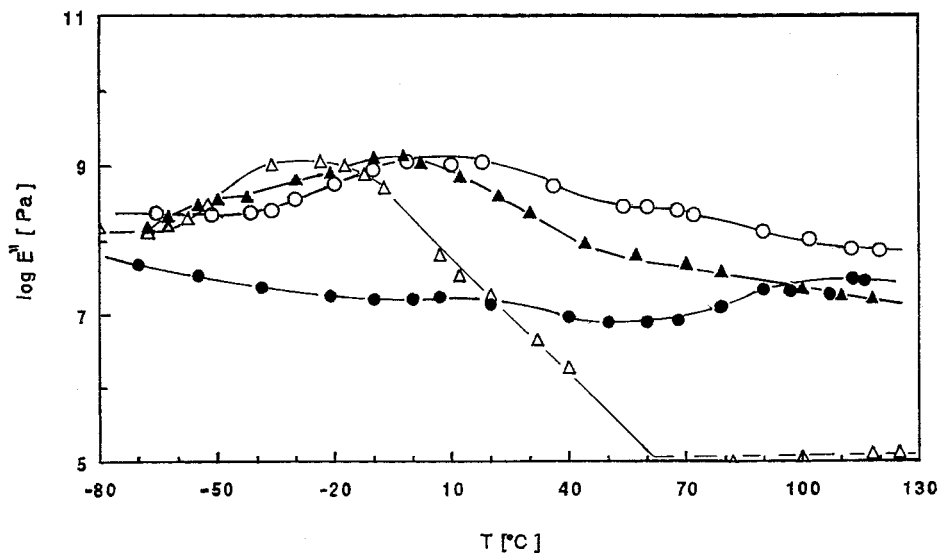


Figure 4 The loss modulus E'' in dependence on temperature. Crosslinked polymer samples are the same as in Figure 2.

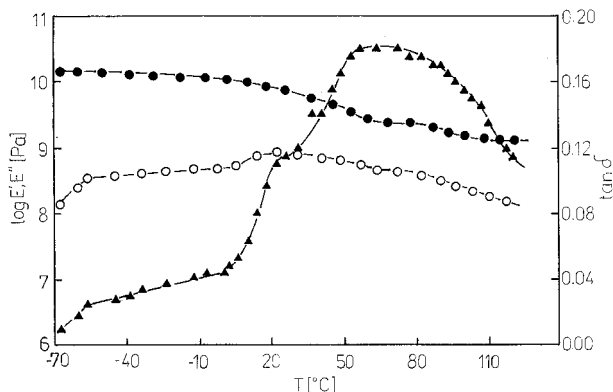


Figure 5 The storage modulus E' (\bullet), loss modulus E'' (\circ), and loss factor $t_g \delta$ (\blacktriangle) in dependence on temperature in the dynamic testing (110 Hz). Crosslinked polymer PETA-PGDAA (3 : 1). Polymer network B_{II} obtained after the photocuring in the second step of synthesis.

dynamic testing than predicted from static tests; and for the calculated M'_c , we obtained nonrealistic, surprisingly low values.

Another influence of the degree of crosslinking on the network properties is a displacement of the damping peak ($t_g \delta$ peak) to higher temperatures and a broadening of the damping peak as the network density increases. The position of the maximum value of $t_g \delta$ is mostly defined as T_g . The relatively low T_g values observed for highly crosslinked networks used in this study (Table VI) can be attributed to the residual unsaturation. The dangling functional groups in networks that were synthesized from monomers with the high density of functional groups have a tendency to hamper the segmental organization. This can be improved by the thermal curing. The T_g of sample C_{II} after thermal treatment at 200°C increased considerably (Fig. 3). On the other hand, the M'_c higher of two decimal orders pointed out a decrease of crosslink density. This fact and the observed one narrow peak for C_{II200} instead two broad peaks for C_{II} in the $t_g \delta$ thermal spectrum indicates a partial thermooxidative destruction of the primary formed crosslinks and restructuralization of the network from a two-phase to a one-phase system. Nevertheless, the substantially higher values of T_g (175–240°C) were observed for polyacrylate networks based on multifunctional monomers also including the PETA polymer network³⁰ and dimethacrylates.⁷

The broad damping curves in Figure 3 and 5 for networks C_{II} and B_{II} show, besides the main peak, also another small one. More than one peak

on the $t_g \delta$ dependencies indicate that the network structure is not a simple homogeneous type, and the crosslinked polymer B_{II} and C_{II} probably consists of two differently crosslinked phases. This finding is consistent with the results obtained from FTIR and sol–gel analysis. Inhomogeneities in crosslinked polymers were predicted also by the model calculation⁸ and described in experimental studies of free radical crosslinking copolymerizations.^{15,21,30}

The results from dynamic mechanical measurements are dependent also on the frequency of stress oscillations if the relaxation times of the polymer are longer than the period of oscillation. The damping peak is shifted to higher temperatures as the frequency is increased. Typical results are about a 7°C shift for each one decimal order increase in frequency.⁴⁴ The values for T_g determined at 11 and 110 Hz presented in Table VI show higher differences for highly crosslinked samples (A_{200} and C_{II200}). The changes of T_g due to a frequency for most of the further samples are very close to a predicted increment.

Finally, the stress–strain measurements were used to determine M'_c for selected samples using equation

$$F = A_o \frac{\rho RT}{M'_c} (\alpha - 1/\alpha^2)$$

where F is a force, α is an extension, A_o is a cross-sectional area of underformed sample, and ρ is a density of polymer.

The M'_c values were determined only for networks prepared from PETA–PETAA 2 : 1 (sample 2) and 5 : 1 (sample 5), and PETA-PGDAA 1 : 1 combinations (sample A).

The other samples cannot be evaluated in the same way for the difficulties in cutting perfect testing specimens. M'_c were calculated using the values of stress and strain at peak (an average from four specimens). M'_c for sample 2 is 480, for sample 5 is 900, and for sample A is 1100 [g/mol]. The M'_c values calculated from stress–strain measurements that are not influenced by solvent–polymer interaction parameter χ agree well with values of M_c obtained via the swelling experiments and approximate values of χ .

We would like to point out that the networks synthesized from multifunctional monomers lead often to a nonuniform course of the reaction. The functional groups simultaneously to the main polymerization reaction are consumed in the side

reactions. The microheterogeneities originated in this way cause the fluctuation in crosslink density and the chemical composition in synthesized polymer. So the polymerization conditions of multifunctional monomers influence considerably the final properties of the networks prepared even from the same batch composition.

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