Networks of Photocrosslinked Poly(meth)acrylates in Linear Poly(vinyl chloride)

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ABSTRACT: Five different multifunctional acrylic monomers (trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, and dipentaerythritol pentaacrylate) were photopolymerized alone or in a matrix of linear poly(vinyl chloride) (PVC) with 2,2-dimethyl-2-hydroxyacetophenone as a photoinitiator. The course of photopolymerization was estimated with Fourier transform infrared spectroscopy. The amount of insoluble gel formed during photopolymerization was determined gravimetrically. The crosslinked poly- merization of pure monomers was much faster than that in the presence of PVC. However, the efficiency of the reaction was higher when it was carried out in a PVC blend because of the higher mobility of the propagating macroradicals. The influence of the monomer structure and functionality on the polymerization course was examined. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3725–3734, 2002

Key words: photopolymerization; crosslinking; poly(vinyl chloride) (PVC)

INTRODUCTION

Two or more mixed, crosslinked polymers form an interpenetrating polymer network (IPN). When one of the components is completely linear, such a composi- tion is called a semi-IPN. An especially high degree of crosslinking can be achieved with multifunctional monomers.[1,2]

In many cases, IPNs do not interpenetrate com- pletely on a molecular level. Therefore, phase separa- tion on a nanometer scale can occur. The properties of IPNs depend not only on the chemical structure of interpenetrating polymers but also on the crosslinking degree, the physical entanglement of chains, and the bulk morphology (domain sizes and their distribu- tion). They are characterized by insolubility, good me- chanical properties, and chemical and thermal resis- tance.

There are several ways to obtain typical IPNs and semi-IPNs, including the simultaneous polymeriza- tion of two monomers or the synthesis of one polymer in the matrix of a second one.[1] A fast and easy method of network synthesis is photoinduced polymerization (photocuring), which takes place mainly in thin sur- face layers contrary to a reaction caused by high- energy radiation or high temperatures.[2–4] This means that the heterogeneity of a photopolymerized blend, in addition to its nonmiscibility, also influences the dif- ferent degrees of conversion with different sample depths.

The kinetics of photopolymerization[5–16] and the ef- ficiency of different photoinitiators[17–21] have been studied in various acrylate and methacrylate systems. Moreover, the general mechanism of the reaction (in- cluding the initiation, propagation, and termination processes) is well known.[3,14–16,22] Kinetic models of the photoinitiated polymerization of (meth)acrylates often assume the same reactivity of the double bonds, and this is not true for multifunctional monomers forming highly crosslinked networks. Moreover, in theoretical considerations, one assumes that the initi- ator efficiency is constant over the course of the poly- merization; in fact, it decreases continuously because radical recombination is more probable where envi- ronmental viscosity increases. The progress of the photopolymerization of multifunctional monomers is connected to the formation of three-dimensional net- works, in which unreacted groups or monomer mol- ecules can be trapped. Usually, at the beginning of the synthesis, autoacceleration is observed as a result of the limited mobility of propagating chains. In further steps of the reaction, when the reactivity of macroradi- cals is diffusion-controlled, the polymerization rate decreases. It is generally accepted that in such cases, the termination is a monomolecular or bimolecular process. In practice, a mixed termination mechanism occurs.

The structure, porosity, and reactivity of multia- crylic polymers and copolymers were intensively studied by Kolarz and coworkers.[23–27]

IPNs have found many applications as automotive parts (tires, belts, and bumpers), hoses, cables, gaskets, damping compounds, ion-exchange resins, optical fibers, medical gears, artificial teeth, and dental fillings.

Their advantages, including high process speeds, low energy consumption (no heating), and low production costs, are the main reason for the fast development of radiation technologies. However, not all the properties of photocured products are satisfactory, so basic investigations in this field are necessary.

The aim of this work was to obtain semi-IPNs with five different multifunctional monomers (acrylates and methacrylates) by photopolymerization in the presence of linear poly(vinyl chloride) (PVC) and to compare the kinetics and efficiency of the process. These photocrosslinked polymer blends were prepared for further studies of their properties, especially their thermal and photochemical stability, and these studies are now in progress.

EXPERIMENTAL

Chemicals

PVC (Anwil, Włocławek, Poland) was precipitated from a 2% polymer solution in tetrahydrofuran (THF; 2% wt) by methanol. Separated PVC powder was accurately dried in a vacuum drier at room temperature. The polymer purity was checked by Fourier transform infrared (FTIR) spectroscopy.

The monomers (Aldrich, Milwaukee, WI) were trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), pentaerythritol triacrylate (PETA), pentaerythritol tetraacrylate (PETeA), and dipentaerythritol monohydroxypentaacrylate (DPEPA). The photoinitiator was 2-hydroxy-2-methyl-1-phenylpropanone (Darocur 1173, Ciba–Geigy, Basel, Switzerland). The solvent was THF (Aldrich). The monomers, photoinitiator, and solvent were used as received. The structures of the monomers and photoinitiator are shown in Scheme 1. The main monomer features are presented in Table I.

Preparation of the IPNs by photopolymerization

We used a simple method of IPN preparation: the monomer and photoinitiator were mixed with a solution of a linear polymer (PVC) in THF. The weight ratio of the monomer to the polymer was 1:1. The concentration of the photoinitiator in the polymer was 5 wt %. Mixed solutions were poured directly onto KBr windows or pure polyethylene support films (the polyethylene used was characterized by complete transparency in the range of double-bond appearance). After solvent evaporation and drying, films were UV-irradiated for polymerization. A comparison of the polymerization course for compositions with different monomers was made on films of the same thickness (10 μm). The course of the reaction was monitored by FTIR spectroscopy.

Conditions of UV irradiation

The photopolymerization was carried out on a high-pressure mercury vapor lamp (HPK 125W, Philips, Eindhoven, The Netherlands) in an air atmosphere at room temperature (20°C). The distance of the sample from a light source was 10 cm, and the intensity of the incident light was 31.1 mW/cm^2.

Infrared analysis

An infrared analysis was carried out with a Genesis II (Mattson Instruments, Madison, WI) FTIR spectrophotometer equipped with the WINFIRST computer program. The absorbance at 810 cm^{-1}, attributed to out-of-plane deformation vibrations of double bonds in the monomer, was used to estimate the conversion degree during photopolymerization. The details of the calculation were published previously.[28,29]

Gel analysis

The gel amount was estimated gravimetrically by a solvent (THF) treatment of the sample and by the weight of the insoluble fraction after its separation and drying. Each estimation was repeated three times, and the average value was calculated. The separated gel was analyzed by FTIR in the form of pellets with KBr, and these spectra were compared with spectra of the sample before separation (i.e., containing both soluble and insoluble parts).

Additionally, an elemental analysis of gel was performed, and the amounts of C, H, O, and Cl were compared with the amounts of these elements in non-separated networks.

Elemental analysis

The elemental analysis was performed by a conventional burning technique with a Heraeus furnace (Hanau, Germany). The 0.2–0.3-mg sample was combusted in an pure oxygen stream at 700°C. Formed CO$_2$ and H$_2$O were absorbed in manganese perchlorate and ascarite, respectively. The chlorine amount, after a 5–10-mg sample combustion in oxygen, was determined by solution titration by mercuric nitrate according to a known procedure.[30] The results are reported as element weight percentages.

RESULTS AND DISCUSSION

Photopolymerization of pure multifunctional (meth)acrylates

The reactivity of the composition depends on the functionality and chemical structure of the monomer, its
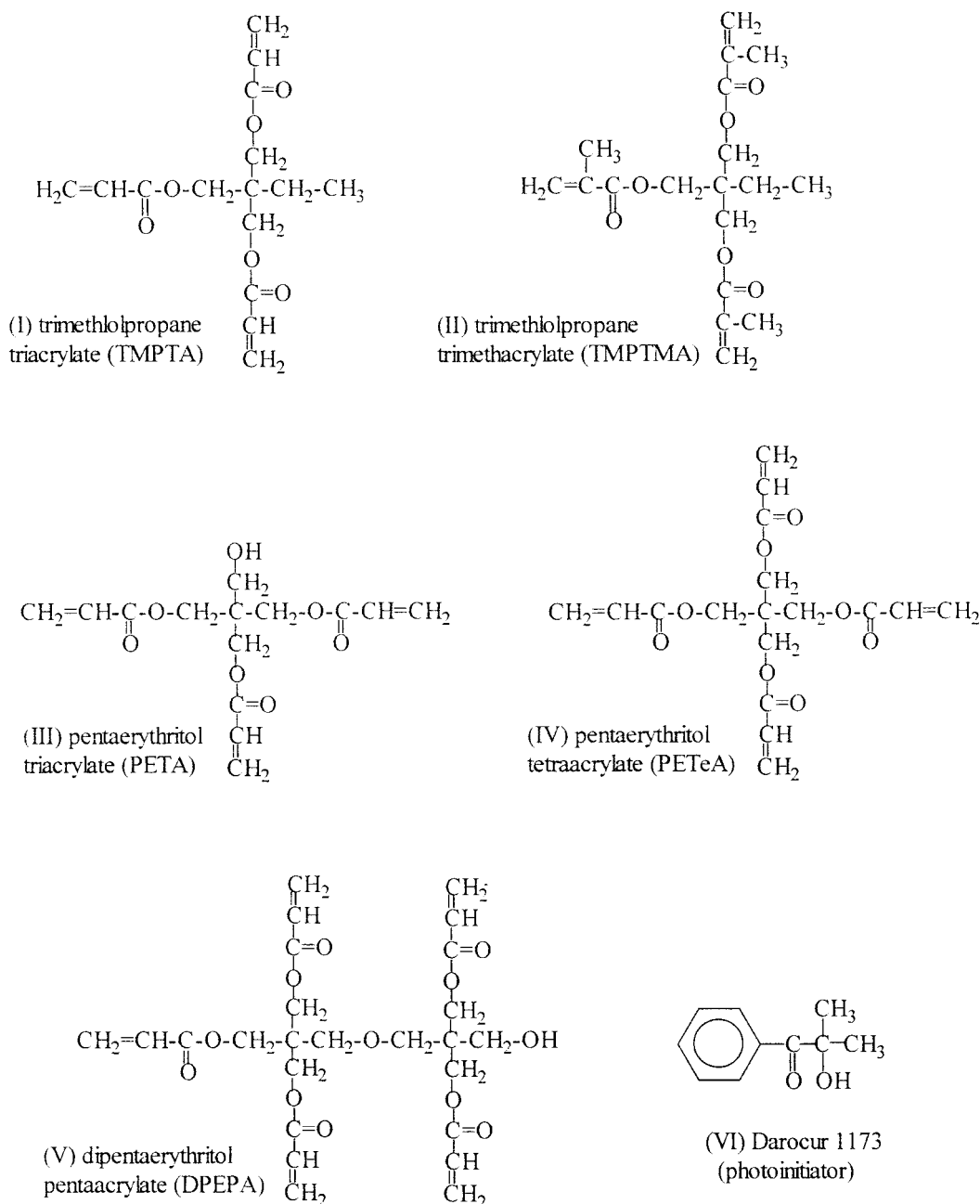
Scheme 1 Chemical structures of the monomers (**I–V**) and photoinitiator (**VI**).

viscosity, and the reaction conditions (the temperature, irradiation intensity, presence or absence of oxygen, and type and concentration of initiator). These factors influence the kinetic parameters, such as the initiation, propagation, and termination rate constants. Because the compared reactions occurred under identical conditions and in the presence of the same amount of the added initiator, the changes in the polymerization course arose only from the chemical and physical differences between the monomers. The characteristics of the monomers are shown in Table I. The monomer functionality, defined as the number of double bonds per molecule, varied from 3 to 5. Func-

tionality can also be expressed as the number of double bonds per kilogram of monomer (Table I): this value was lowest for TMPTMA (8.88) and highest for PETeA (11.36). All the monomers contained tertiary carbon atoms and one to three pendant functional groups of the same size. A common feature was the rank value, which was three atoms between consecutive functional groups, with the exception of DPEPA, which had three or seven atoms between acrylic groups.

The monomers had different branching degrees, and DPEPA had the highest. Two monomers, PETA and DPEPA, contained additionally hydroxyl groups

TABLE I
Characteristics of (Meth)acrylic Monomers Used

| Sample | Molecular weight (g/mol) | Functionality | | Number of pendant functional groups | Rank |
		Number of C=C per molecule	Number of C=C per 1 kg		
TMPTA	296	3	10.13	1	3
TMPTMA	338	3	8.88	1	3
PETA	298	3	10.07	1	3
PETeA	352	4	11.36	2	3
DPEPA	524	5	9.54	3	3; 7

built on one end of the molecule; TMPTA and TMPTMA had ethyl (—CH$_2$CH$_3$) groups attached to chains. Only DPEPA distinguished the presence of an oxygen atom inside the molecule backbone (besides oxygen atoms in acrylic groups).

Figure 1 shows the conversion of double bonds (X) versus the time of photopolymerization (t) for pure multifunctional (meth)acrylates (TMPTA, TMPTMA, PETA, PETeA, and DPEPA) containing 5% photoinitiator. These monomers underwent a fast polymerization process on a polychromatic UV lamp. The rate of reaction (R_p) in a determined period could be calculated from the slopes of the straight-line segments of these curves. The actual rate at any time could be read from the curves obtained by the differentiation of the relations in Figure 1 and the multiplication of the dX/dt derivative by the monomer functionality.

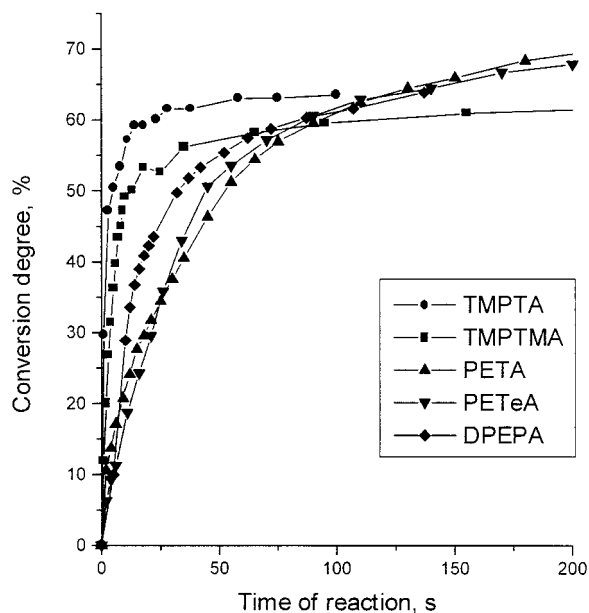The polymerization in pure monomers began immediately after the lamp was switched on and was fastest in the beginning of the process. In all these cases, the induction period was not measurable (if it occurred, it was shorter than 1 s), although an experiment was carried out in the presence of atmospheric oxygen, an inhibiting agent.[2,31] The maximum rate (R_p^{max}) in TMPTA, TMPTMA, PETA, and PETeA was reached just after onset, but only in DPEPA was 10 s of UV irradiation needed to obtain R_p^{max}. In this last case, the conversion–time curve had a typical S shape, and the inflection point corresponded to the maximum on the differential curve. The maximal values of the photopolymerization rate (R_p^{max}) are listed in Table II. Reaching R_p^{max} quickly was possible in very thin films. The UV radiation easily penetrated thin layers, and initiation occurred in the whole sample, whereas for thick films, the reaction started close to the surface and was very inhomogeneous.

R_p changes as a function of time for TMPTA and DEPA (monomers characterized by an extreme reaction speed) are presented in Figure 2. For TMPTA, in which R_p^{max} was highest, a very sharp peak was observed. TMPTMA, PETA, and PETeA exhibited a similar tendency in R_p–time curves, whereas this relation in DPEPA was different: the maximum was broader and flat. In the latter, the lowest R_p^{max} value was found. The smallest polymerization rate in DPEPA was caused by fast crosslinking due to five functional groups per monomer molecule. It seems that the number of pendant groups, highest in DPEPA (3; see Table

Figure 1 Degree of conversion as a function of time for pure multifunctional monomers polymerized in air at room temperature on an HPK lamp with 5 wt % Darocur 1173 as a photoinitiator.

TABLE II
R_p^{max} and Corresponding Conversion Degree (X) in Pure Meth(acrylate)s and in Their Blends with PVC (Calculated from Differential Curves of Conversion)

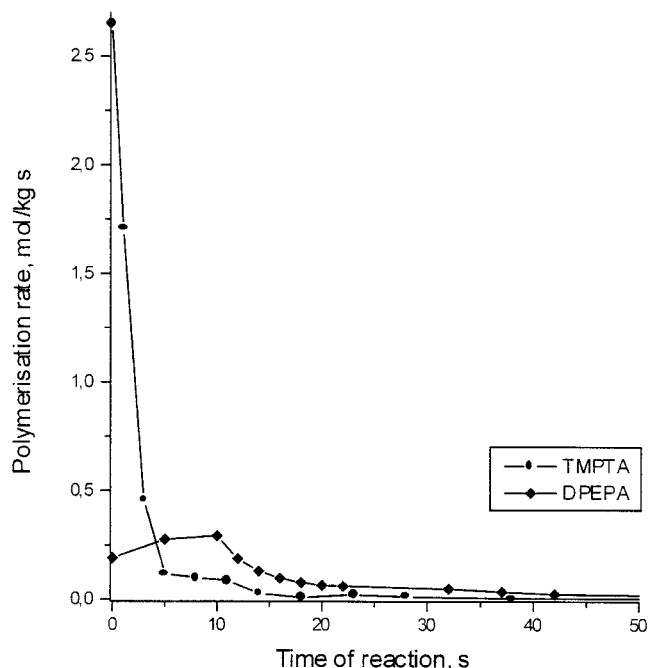| Sample	$R_p^{max} \times 100$ (mol kg^{-1} s^{-1})	X (%) corresponding to R_p^{max}
TMPTA	264.71	29.8
TMPTMA	120.55	11.9
PETA	53.37	6.2
PETeA	35.44	10.6
DPEPA	29.20	28.9
TMPTA–PVC	1.67	9.9
TMPTMA–PVC	1.63	5.5
PETA–PVC	0.36	0.7
PETeA–PVC	2.84	15.9
DPEPA–PVC	5.53	34.8

Figure 2 Changes in the polymerization rates for two monomers, TMPTA and DPEPA, versus the reaction time.

I), also influenced the high crosslinking degree and retardation of the reaction. The influence of pendant groups causing hindrances and blocking the free rotation of remaining functional groups was discussed in detail in a publication by Dietz et al.[32] It is interesting that in the fastest (TMPTA) and slowest (DPEPA) processes, the conversion degree at the maximum rate reached a similar value of about 29–30% (Table II), whereas in other formulations, the conversion degree attributed to R_p^{max} was more than two times lower.

Comparing the polymerizations of two similar monomers, TMPTA and TMPTMA, one can notice that in TMPTMA the maximal speed was more than two times lower than that in TMPTA. Both monomers had three functional groups in molecules, but the functionality calculated per kilogram was lower in TMPTMA than in TMPTA (Table I). A similar relation was reported previously for difunctional monomers by Kurdikar and Peppas[8] and Jager et al.[33] Kinetic data provide evidence that multifunctional methacrylates with UV polymerize more slowly (the propagation constant has a lower value) than acrylate analogues.[34] Because of the similarity of the structures of TMPTA and TMPTMA, the difference in the polymerization rate could be explained by steric hindrances of methyl groups neighboring reactive double bonds. Another reason could be the higher stiffness of the methacrylate molecules and their lower mobility in comparison with acrylates.[35] Moreover, methacrylate polymerization is characterized by a lower sensitivity to oxygen inhibition.[36]

The next monomers reacted more slowly, and the rate of their polymerizations could be ordered as follows:

$$TMPTA > TMPTMA > PETA$$
$$> PETeA > DPEPA \quad (1)$$
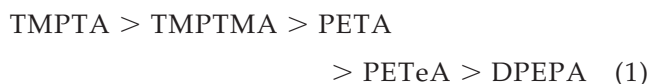
The intermediate R_p^{max} values in TMPTMA, PETA, and PETeA arose from the number of reactive groups (three or four). Recently, it was found that the presence of a heteroatom in a monomer greatly affects polymerization in air. Di(meth)acrylate monomers containing oxygen or sulfur are less sensitive to oxygen inhibition, and this accelerates the propagation rate.[31,35] However, we did not observe the influence of oxygen atoms in DPEPA on its photopolymerization: the maximal reaction rate was lower than that of other monomers. There were other differences in the chemical structures of the compounds used that decided the polymerization course.

It is necessary to add that the viscosity of these monomers was very high (TMPTA had a somewhat lower viscosity than the others). The high viscosity restricted the diffusional mobility and decreased the reaction rate. It also hampered oxygen diffusion to growing macromolecules, and so oxygen inhibition was reduced. Therefore, two opposite effects influencing the polymerization rate occurred simultaneously.

For PETA, which had approximately the same functionality as TMPTA, the retarding effect of hydroxyl groups could be seen. Perhaps some hydrogen bonds [eq. (2)], which were formed between OH and C=O from acrylate groups, hampered the mobility of the monomer and additionally increased its viscosity:

$$(2)$$
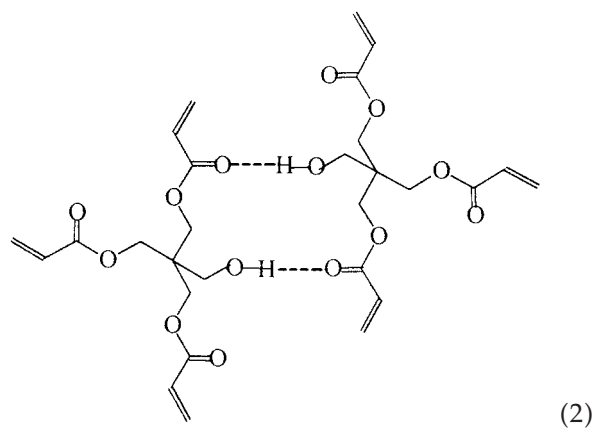
After reaching the maximum, the rate of photopolymerization dropped considerably in all specimens during the next few seconds of UV irradiation. This drop was caused by gelation and the trapping of propagating radicals in the formed networks. After a def-

inite time of reaction, the rate of polymerization decreased even to 0, and the conversion degree reached a plateau. The hard, transparent films were formed just after a few tens of seconds in all cases.

Very high polymerization rates at the beginning of the reaction provided evidence that an autocatalytic effect, which was previously described in the literature,[31,32] took place. This effect was caused by the hampering of diffusion-controlled termination. Sometimes, intermediate species, markedly influencing the polymerization rate, were also formed.

As photopolymerization progressed, the autodeceleration effect was observed because at higher conversions, the propagation also became a diffusion-limited step.

Although there were significant differences in the beginning rates of polymerization, after somewhat longer periods of UV irradiation, the conversion degrees reached similar values; for example, in all cases, it equaled about 60% after 100 s (Table III).

Growing macroradicals differ markedly in their reactivity. Free and mobile radicals react very quickly with monomers, but radicals trapped in the network are not able to further react. In the photopolymerization of multifunctional monomers, a gel is formed very early in the beginning of the process, so a lot of trapped radicals and unreacted double bonds are present in the network. The amount of gel formed during the photopolymerization of TMPTA, TMPTMA, PETA, PETeA, and DPEPA after 25 and 50% conversions is presented in Table IV. In most of the pure monomers, the gel amount was higher then the conversion degree. It is obvious that not all the functional groups from the monomers took part in polymerization. Even if only one or two of them reacted, highly branched and entangled networks were formed, and the polymers became insoluble. After gelation, the reaction rate decreased because the diffusion of reactive chain ends was strongly limited.

The relatively small amount of gel found in polymerized TMPTMA indicated that methyl groups in this monomer inhibited gel formation.

TABLE III
Conversion Degree in Meth(acrylates) after 100 s and in Their Blends with PVC (1:1) After 1000 s of Photocuring
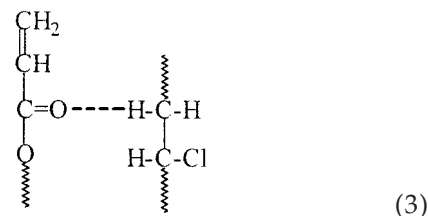
Sample	Time(s)	Conversion degree (%)
TMPTA	100	63.5
TMPTMA	100	59.8
PETA	100	60.9
PETeA	100	61.7
DPEPA	100	63.0
TMPTA–PVC	1000	78.5
TMPTMA–PVC	1000	65.0
PETA–PVC	1000	33.5
PETeA–PVC	1000	74.0
DPEPA–PVC	1000	78.1

TABLE IV
Gel Amount Formed in Meth(acrylates) and Their Blends with PVC (1:1) After Different Degrees of Conversion

|	Gel amount (%)	
Sample	After 25% conversion	After 50% conversion
TMPTA	79.10	96.73
TMPTMA	24.00	39.30
PETA	47.25	77.92
PETeA	71.60	86.08
DPEPA	76.31	89.22
TMPTA–PVC	55.63	64.05
TMPTMA–PVC	31.09	50.10
PETA–PVC	27.03	41.14
PETeA–PVC	29.07	48.75
DPEPA–PVC	41.55	59.65

Photopolymerization of (meth)acrylates in the presence of pvc

The second part of our experiment concerned the photopolymerization course in a PVC matrix. All semi-IPNs obtained in this way were much more flexible than those without PVC, but they were a little opaque, and this was the first evidence for nonmiscibility. However, the Hildebrand parameters (δ) of PVC and poly(methyl methacrylate) [PMMA; chosen as a model polymer for the poly(meth)acrylates studied], which were equal 19.34 and 18.58 $(J/m^3)^{1/2}10^3$, respectively,[37] did not give a clear answer about miscibility. Complete miscibility occurs when the solubility parameters are similar, and according to Hansen's theory, specific interactions have to be similar in both polymers, so the δ components characterizing dispersive interactions (δ_d), dipole–dipole interactions (δ_p), and hydrogen bonding (δ_h) should also be the same. The miscibility of polymers strongly depends on their average molecular weight, its distribution, and tacticity. The reports in the literature are not always consistent about the miscibility of PMMA/PVC,[38–42] but strong, specific interactions between both types of macromolecules were proved:

$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ C=O \text{----} H\text{-}C\text{-}H \\ | \quad\quad\quad\quad | \\ O \quad\quad\quad H\text{-}C\text{-}Cl \end{array} \qquad (3)$$

The poly(meth)acrylates studied should exhibit similar interactions with PVC chains.

For polymerization in a PVC matrix, the following order of rates (R_p^{max}) was observed:

DPEPA + PVC > PETeA + PVC > TMPTA

+ PVC > TMPTMA + PVC > PETA + PVC   (4)
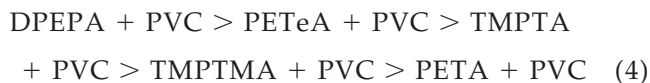
The dilution of the monomer by PVC (the ratio of the monomer to PVC was 1:1) changed the order of rates previously found for pure monomers. Generally, an increase in the C=C number in the monomer molecule accelerated the polymerization process in the blend with PVC. The exception was PETA–PVC, for which the lowest rate was observed. This could have been caused by the presence of a mobile hydrogen atom in the polarized O—H bond, which inhibited polymerization. It also seems probable that, besides the reactivity of this hydrogen atom, its participation in a specific interaction with PVC additionally hampered monomer reactivity:

(5)

(6)
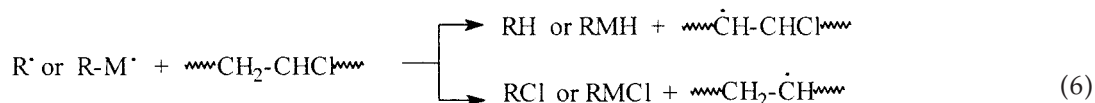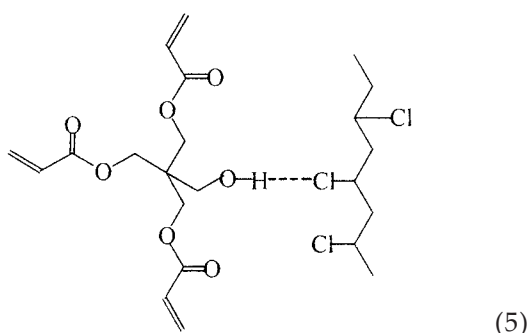
where R · is the free radical from the initiator and R—M · is the growing macroradical. It is especially easy to abstract H or Cl placed in structural defects always present in PVC (e.g., branching points, head-to-head structures, and allyl or ketone groups). In PVC, allyl groups or allyl radicals (created with UV)

Although the effect of a heteroatom built into the monomer backbone was not observed in the photopolymerization of pure DPEPA, it can partially explain the higher speed of the DPEPA reaction in the presence of PVC. According to Andrzejewska's suggestion,[31,35] ether groups considerably increase the rate of polymerization in an air atmosphere. This was explained by oxygen consumption in a reaction with a methylene group attached to a heteroatom (in which hydrogen atoms are more mobile).

The gel amount (Table IV) indicated that the crosslinking degree was relatively high, although this process was not so fast as in the absence of PVC. It was 27–55% after 25% monomer conversion and 41–64% after 50% conversion, depending on the formulation. At the same time, PVC alone did not undergo photocrosslinking yet (up to 1 h of UV irradiation).

The lower reaction rates and conversion degrees in a PVC matrix (after the same time of UV irradiation) compared with those for pure (meth)acrylates polymerized (Fig. 2 and Table II) can be explained by the chain-transfer reaction [eq. (6)]. It was possibly due to the abstraction of mobile hydrogen or chlorine atoms in PVC by growing macroradicals. Also, small initiating radicals from Darocur photolysis can react with PVC, and this can lead to a decrease in the initiation rate:
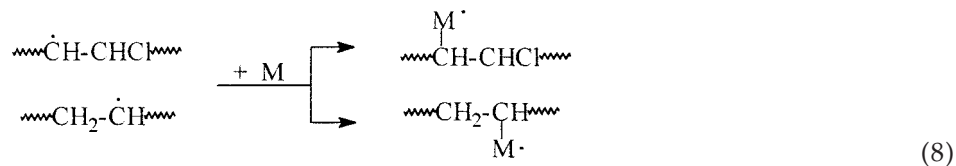
are usually present in which H atoms are very susceptible to abstraction. Allyl macroradicals are relatively stable because unpaired electrons are delocalized [eq. (7)], so they can live much longer than simple primary or secondary alkyl radicals:

(7)

Besides the reaction between radicals and PVC molecules, photoinduced reactions in PVC take place because it is a photounstable polymer.[43] The main photoreactions occurring in PVC are dehydrochlorination leading to polyene formation, accompanied by HCl evolution, chain scission, branching, crosslinking, isomerization, cyclization, and oxidation (in the presence of oxygen).[43] The results of PVC photodegradation are evolved chlorine atoms, which are known as very mobile, nonspecific, highly reactive radicals. They can participate in substitution, which usually occurs in alkanes or in an addition reaction typical for

unsaturated organic compounds.[44] These radical atoms are probably responsible for an efficient deactivation of propagating macroradicals in a recombination process. Moreover, HCl formed during PVC dehydrochlorination also takes part, in addition to double bonds, either in the monomer or in the poly(meth)acrylate (where not all functional groups are consumed).

However, created by UV radiation, radicals located on PVC chains are new active centers that can further react with a monomer [reaction (8)]. Some of them are long-living, and this increases the probability of reac-

tion with slowly diffusing monomers or polymer segments containing unreacted functional groups. In PVC, especially durable are polyene radicals [—(CH═CH)$_n$—ĊH—] because of their resonance stabilization [similarly shown in reaction (7) for allyl radicals]. It seems that the concentration of polyenes is relatively low after such a short time of UV irradiation but probably enough for propagation progress. Even in a very rigid network, in which chain translation is not possible, some ends of macromolecules, because of their mobility, can slowly diffuse to reactive places. In a PVC matrix, the mobility of crosslinked chains in formed networks is much higher than in pure poly(meth)acrylates:

$$\underset{\text{ww}\dot{C}H\text{-CHCl}\text{ww}}{\overset{\text{ww}CH_2\text{-}\dot{C}H\text{ww}}{}} \quad + M \quad \longrightarrow \quad \underset{\text{ww}CH\text{-CHCl}\text{ww}}{\overset{M^\cdot}{}} \quad \underset{\text{ww}CH_2\text{-}\underset{M^\cdot}{C}H\text{ww}}{} \tag{8}$$

where M is the monomer molecule. In this way, a grafted polymer is formed in which, besides the physical entanglement of macrochains, covalent bonds between PVC and poly(meth)acrylate exist. Grafting is also the result of normal recombination between macroradicals of both components.

The gel amount estimated in our binary mixtures after longer reaction times (2000 s) was 94–98% in all samples besides PETA–PVC (for which the gel content was 84%). Under the assumption that all the monomer was fully built into the network (even if some double bonds remained unreacted), the grafting degree of PVC was estimated to be 88–96 and 68% in PETA–PVC. The final conversion and plateau on the curve in Figure 3 were not reached even after 3000 s of UV irradiation.

The formation of covalent bonds between poly(trimethylolpropane triacrylate) and PVC during photopolymerization was previously confirmed by measurements of the glass-transition temperature, which in the semi-IPNs was significantly higher than that in the pure components.[28,29]

Additionally, an elemental analysis was performed to support the conclusion concerning a high grafting degree (Table V). The amount of PVC in a network after 2000 s of UV irradiation was estimated on the basis of the chlorine content. The calculated amount of Cl in pure PVC was 56.8 and 27.03% in the starting blend (the formulation was 50% PVC, 50% poly(meth)acrylate, and 5% initiator). It was clearly seen that the amount of PVC in an insoluble gel was only somewhat lower than in a nonseparated network. It varied from 37.0 to 48.4%; therefore, the grafting degree was approximately 74–97%. Somewhat smaller values than those estimated on the basis of the gel amount probably arose from the partial dehydrochlorination of PVC. Here again, the lowest PVC amount (37%) and grafting degree (74%) were found for PETA–PVC, but this value was slightly higher than that estimated previously. We suppose that grafting strongly competes with polymerization.

Because of the very low speed of monomer polymerization in PVC, a longer time of reaction (1000 s) was chosen for a comparison of the conversion degrees (Table III). The order of the conversion degrees after 1000 s was as follows:

$$\text{TMPTA–PVC} > \text{DPEPA–PVC} > \text{PETeA–PVC}$$
$$> \text{TMPTMA–PVC} > \text{PETA–PVC} \tag{9}$$
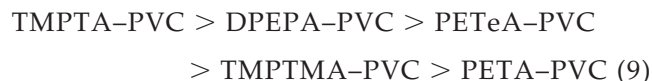
The higher the number was of functional groups, the higher the conversion degree was (with the exception of TMPTA). This set differs from the order of rates shown previously [inequality (4)] by the position of TMPTA: the highest conversion degree was observed for the polymerization of this monomer in PVC, but its maximal rate was intermediary.
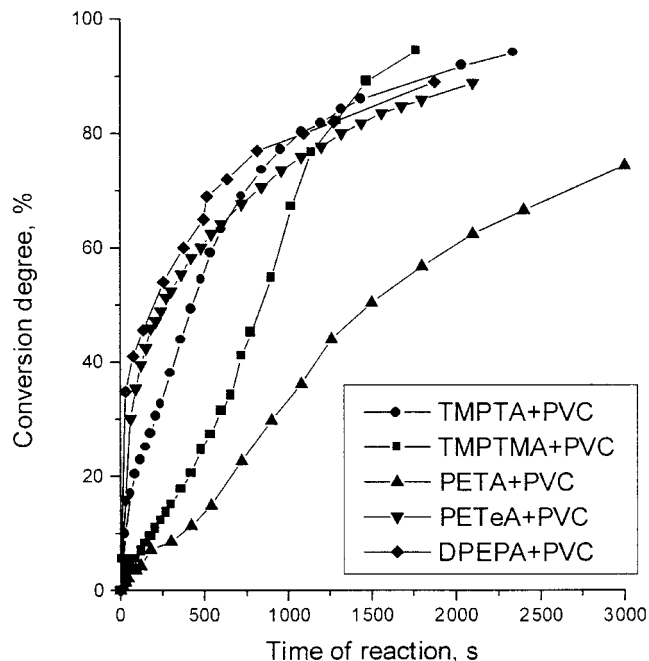

Figure 3 Degree of conversion as a function of time for multifunctional monomers polymerized in a PVC matrix (under the same conditions listed in Fig. 1).

TABLE V
Grafting Degree Estimated on the Basis of Chlorine
Content in a Network of Meth(acrylates) with
PVC (1:1) After 2000 s of UV Irradiation

Sample	Separated gel		Grafting degree of PVC (%)
	Cl content (%)	PVC content (%)	
TMPTA–PVC	26.2	48.4	96.8
TMPTMA–PVC	23.9	44.2	88.4
PETA–PVC	20.0	37.0	74.0
PETeA–PVC	24.5	45.3	90.6
DPEPA–PVC	25.3	46.8	93.6

However, even after such a long time of reaction (1000 s), the plateau in the conversion degree in some cases was not reached. Although the reaction rates were very low in these cases, the conversion degree approached 90% or more after a longer reaction time (i.e., after about 1 h; see Fig. 3). Such a high final conversion was not achievable in the polymerizations of pure monomers, for which it did not exceed 80% even after a few hours of exposure to UV.

During the photopolymerization of (meth)acrylates in a PVC matrix, the autocatalytic effect was also observed. The reaction rate showed a tendency to slow down after reaching the maximum.

In radical polymerization, the posteffect (occurring even in the dark) should be considered. In our systems, we found a further slowing of the reaction of double bonds in poly(meth)acrylates mixed with PVC, but 100% double-bond conversion was not obtained in any case. The concentration of unreacted groups in pure poly(meth)acrylates was approximately constant during storage at room temperature. These differences could be explained by the different structures of the networks. In a PVC matrix, crosslinked poly(meth)acrylates are separated by linear or only slightly bonded PVC chains, and so the macromolecule mobility is higher and facilitates further reactions of unreacted double bonds. In pure poly(meth)acrylates, networks are more rigid, and trapped radicals have no possibility to escape and react.

Another factor that enabled further polymerization was a delay in volume shrinkage. Fast polymerization at the initial stage led to a nonproportional volume reduction. In other words, the conversion degree joined with crosslinking overtook the volume change. The mobility and reactivity of segments containing unreacted double bonds in such quickly created network were markedly higher than in specimens subjected to relaxation. We suppose that this effect could also take place in formed semi-IPNs based on PVC and was the reason for high R_p^{max} values (Table II) as well as high double-bond conversions (Table III) in the presence of PETeA and DPEPA. The influence of pendant groups on the delayed shrinkage has been described in the literature.[32]

As mentioned in the beginning of this subsection, the components in the network, by analogy to the PMMA/PVC blend, can be miscible. The high degree of grafting additionally changes the interaction between the components (which are nonbonded by covalent bonds; such polymers exists as a minority). The formed grafted polymer can act as a typical compatibilizer, improving miscibility. The rearrangement of macromolecules in such densely crosslinked networks is difficult because of the restricted mobility, so miscibility enhancement is probably negligible.

CONCLUSIONS

The photopolymerization of the pure (meth)acrylic monomers studied was characterized by a high initial rate and fast gelation due to the formation of crosslinked networks. The results indicated that besides high viscosity and the functionality, the chemical structure of the monomers also had a significant influence on the polymerization course. The presence of hydroxyl groups participating in hydrogen bonds decreased the polymerization rate. The methyl substituent in TMPTMA reduced the gel amount because of steric hindrances. The final conversion degrees were similar in all the polymerized monomers and did not exceed 70%.

The rate of the photopolymerization of the monomers studied was much lower (by about two orders of magnitude) when the photopolymerization occurred in the matrix of linear PVC. This was caused by an efficient deactivation of propagating macroradicals by PVC macromolecules or chlorine atoms created in the matrix upon UV irradiation. However, in the presence of PVC, a significantly higher conversion degree (>90%) was possible after a longer period of UV irradiation and in postpolymerization.

During the polymerization of the multi(meth)acrylates in a PVC matrix, the chain-transfer reactions took place, which led to PVC grafting, the increase in the gel fraction, and further polymerization of the (meth)acrylates. The presence of linear PVC enhanced the reaction of macroradicals because of its separation by PVC molecules (dilution), which increased their mobility and facilitated the diffusion to chain ends containing double bonds. The longer time needed for the achievement of the final conversion degree indicated that trapped reactive chain ends slowly reacted during network relaxation, but the propagation was efficient.

The proper choice of the monomer and matrix will allow us to design suitable networks according to the application. Monomers with high functionality can be used if very fast curing is needed. Multifunctional monomers can be polymerized in a PVC matrix when a low amount of unreacted double bonds in the final

product is important and high purity or nonreactivity is required.

It should be added that the obtained networks were characterized by a very good adhesion to glass, metals, and plastics (e.g., polyethylene film); this allows us to predict their usage as protective coatings.

We expect that materials obtained on the basis of poly(meth)acrylate/PVC semi-IPNs will have good thermal and photochemical stability as well as chemical resistance, and this is promising for their future applications. Other important features are their hardness and relative flexibility, so semi-IPNs combine the advantages of both components.

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