Methacrylate-based polymer blends containing oligomeric 1,2-polybutadienes

Agnieszka Marcinkowska · Ewa Andrzejewska

Abstract Partly miscible polymer blends with semi-IPNs structure built from polydimethacrylate networks and hydroxyl-terminated liquid polybutadienes with predominant 1,2-structure (LBH) were prepared by photopolymerization method. Photopolymerization kinetics of dimethacrylate–LBH mixtures were monitored by DSC technique under isothermal conditions. Kinetic curves and related parameters, like polymerization rate and degree of double bond conversion were determined as functions of dimethacrylate structure, LBH molecular mass, and its content in the mixture as well as polymerization temperature. The photopolymerization kinetics and activation energy for the polymerization rate were discussed taking into account the phase separation occurring during the curing reaction. The extent of phase separation (based on T_g's measurements) depended on LBH content and dimethacrylate chemical structure. The effect of LBH content on hardness of polymer blends was also examined.

Keywords Polymer blends · Semi-IPN · 1,2-Polybutadienes · Polydimethacrylates photopolymerization kinetics · DSC

Introduction

Interpenetrating polymer networks (IPN) are materials comprising two or more polymer networks, which are at least partially interlaced on a molecular scale, but not covalently bonded to each other and cannot be separated unless chemical bonds are broken [1]. IPNs are an important class of materials attracting broad interest from both the fundamental and application points of view [2, 3]. An interesting variation of IPN networks are semi-IPN networks which refers to a class of IPNs where only one of the polymers is crosslinked. On the contrary to IPN network, in semi-IPN systems individual components can be separated from the polymer network components without breaking chemical bonds, so they are generally mixtures of polymers [1]. In most cases polymers are immiscible, or only partially miscible. Immiscible polymers tend to separate spontaneously into two distinct phases. Factors affecting the morphology of the IPNs are compatibility or thermodynamic interaction between components, kinetics of reaction, composition, mobility of the polymer chain, and polymerization degree at the time of gelation [4–7]. It should be noted that the size of domains occurring in a heterogeneous mixture of polymers is related to the rate of polymerization as well as the interactions between polymers.

A group of polymers used as components of IPNs or semi-IPNs are polybutadienes with predominant 1,4-structure [8–17]. One of the most common investigations is preparation of IPNs [8–11, 13] or semi-IPNs [12] with methacrylic polymers. In a typical procedure hydroxyl-terminated butadiene was reacted with isocyanate, and the resulting polymer was swollen with a methacrylate, dimethacrylate, or mixture of methacrylates of various functionality which was then polymerized to form IPN. Some articles describe polymerization of methacrylates in solid 1,4-polybutadiene matrix [14] or grafting of a methacrylate on the polybutadiene during miniemulsion polymerization [15]. High-shock or high-impact polystyrene was obtained by polymerization of styrene in the presence of 1,4-polybutadiene [16] or by mixing of polystyrene with 1,4-polybutadiene [17].

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An especially interesting group of polybutadienes, not widely investigated so far, are liquid polybutadienes with a high content of 1,2-structure, which are used in the production of rocket fuel [18]. There are only few studies describing mixtures or copolymers of 1,2-polybutadienes with methacrylates [19–21].

Anisimov et al. [19] studied the kinetics of low temperature graft copolymerization of triethylene glycol dimethacrylate (TEGDM) onto an hydroxyl-terminated unsaturated oligomeric butadiene rubber (MW = 3,200) by infrared spectroscopy. The rate of copolymerization increased with TEGDM concentration, and when the mole fraction of TEGDM in formulation reached 0.96 the reaction rate stopped to increase or even began to decrease which can be associated with the increase in viscosity of the copolymerizing system and diffusion limitations on reacting species. The calculated reactivity ratios were 0.8 and 2.7 for TEGDM and polybutadiene, respectively.

Hydroxyl-terminated but hydrogenated 1,2-polybutadienes were used in preparation of UV-crosslinkable (meth)acrylate modified polyurethanes. These materials had excellent properties what made them useful as flexographic printing plates [21].

In our study we undertook studies on further possible applications of liquid 1,2-polybutadienes using them as components of semi-IPNs in combination with polydimethacrylates. The INPs were prepared in situ by photopolymerization of dimethacrylates containing dissolved polybutadienes. To ensure good miscibility with the monomers (ethylene glycol dimethacrylate, EGDM and 1,6-hexanediol dimethacrylate, HDDM) hydroxyl-terminated polybutadienes (LBH) with MW 2,100, 3,000, and 5,000 were used. The study focuses mainly on the kinetics of photopolymerization taking into account the phase separation occurring during the reaction. The main experimental method used in this study was differential scanning calorimetry (DSC). Isothermal DSC (photo-DSC) is one of the two methods (along with FTIR) most widely used for investigation of photopolymerization kinetics [22, 23]. It reflects very accurately the influence of various factors on the kinetics at any reaction stage (on kinetic curves) and enables measurements at a wide temperature range.

Experimental

Materials

Ethylene glycol dimethacrylate (EGDM, Fig. 1) and 1,6-hexanediol dimethacrylate (HDDM, Fig. 1) monomers from Aldrich were purified by column chromatography before use. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, $\lambda_{max} \sim 340$ nm) photoinitiator from Aldrich was used as received. Three hydroxyl-terminated polybutadienes (Krasol LBH) with a predominance of the 1,2-structure were supplied by Kaučuk Co. (now Sartomer Czech). Krasol LBH 2000 (LBH2, MW 2,100), Krasol LBH 3000 (LBH3, MW 3,000), and Krasol LBH 5000 (LBH5, MW 5,000) are liquid low molecular mass polymers (LBH2 x ~ 35, LBH3 x ~ 53, LBH5 x ~ 90, Fig. 1). They are statistical mixtures of different microstructures: 15 % of *cis*-1,4-(vinyl) units 25 % of *trans*-1,4-; and 60 % of 1,2-structural units. They were used without further purification.

Investigated systems

Combination of two dimethacrylates and three polybutadienes gives six investigated systems. In the frame of each system, ten compositions containing 0–90 mass% of LBH in 10 mass% intervals were prepared.

Methods of testing

Reaction rate profiles and conversions were determined by isothermal DSC (Pyris 6, Perkin Elmer). Throughout the experiments the DSC unit was operated isothermally at the selected temperature kept with accuracy ± 0.01 °C. The 5 mg samples were polymerized in open aluminum pans (a diameter 6.6 mm). All photopolymerization experiments were conducted at least in triplicate. The polymerization was initiated by the light of a medium pressure Hg lamp (cobalt–glass filter with transmittance range 300–400 nm and maximum at 366 nm, light intensity 2 mW cm^{-2}) and was carried out in Ar atmosphere. The photoinitiator was used in concentration of 1 mass%. For computations, the heat of polymerization was taken to be 56 kJ mol^{-1} of double bonds [24]. Other details of the experiment were analogous to those described [25].

All the compositions prepared within HDDM/LBH and EGDM/LBH systems and containing the photoinitiator were homogenized in an ultrasonic mixer, in the absence of light to avoid premature polymerization and gave transparent solutions. Viscosities η of the investigated compositions were measured by DV-II + PRO Brookfield Rheometer in the cone/plate shear mode.

Thermal transitions (glass temperatures) of semi-IPNs were measured by DSC (Pyris 6, Perkin Elmer). Sample mass of 10–15 mg was scanned at a heating rate of 20 °C min^{-1}. DSC expression curves were taken by heating the samples in the temperature ranging from −70 to 155 °C.

Samples for hardness testing (15 × 10 × 2.5 mm) were prepared in a steel mould with poly(ethylene terephthalate) (PET) cover to avoid the inhibitory effect of oxygen using a Dymax Light Curing Systems lamp (UV Blue Wave 50). Polymerization was initiated with light of wavelength
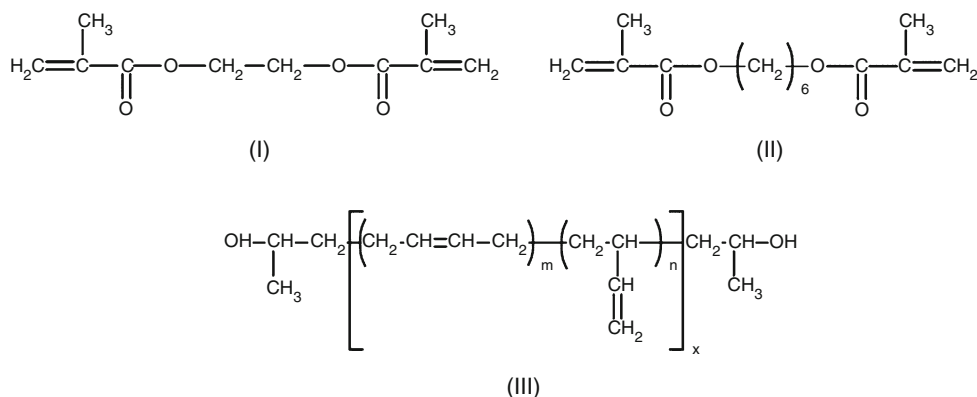
366 nm, so PET, which cuts off short-wavelength UV radiation at about 320 nm did not affect the reaction. Hardness was measured according to standards PN-ISO 868:2004 and PN-EN ISO 527-1:1998 with the use of a Shore (type A) hardness tester (Zwick Roell). The hardness values were the average of at least five measurements.

Results and discussion

Glass transition and phase separation

During the photocuring process the polymerizing monomer/LBH mixtures undergo phase separation driven by the increase in the molecular mass of the growing dimethacrylate polymer and network formation. In general, the phase separation occurring during the polymerization of a monomer dissolved in a nonreactive component is known as *polymerization-induced phase separation.*

In the range of 10–50 mass% of LBH concentrations all the obtained photocured samples are opaque, indicating macrophase separation, which suggests also that the possible copolymerization with polybutadiene double bonds must be rather limited. Above 50 mass% of LBH content the samples become optically transparent indicating their homogeneity or a microphase separation with domain size smaller than the visible wavelengths. According to earlier investigations [26, 27], allylic monomers (which include polybutadienes) copolymerize with methyl methacrylate (MMA) to a limited extent, only when the MMA concentration in the feed is high; their polymerization begins when MMA has already reacted to a large extent. At a low MMA content, allylic monomers practically do not copolymerize. Thus, in our investigated systems we can expect two phases: a polydimethacrylate-enriched phase at higher monomer concentrations in the feed and a LBH-enriched phase when the monomer content is low.

The glass temperatures of the materials containing LBH2 are presented in Fig. 2 as a function of the LBH2
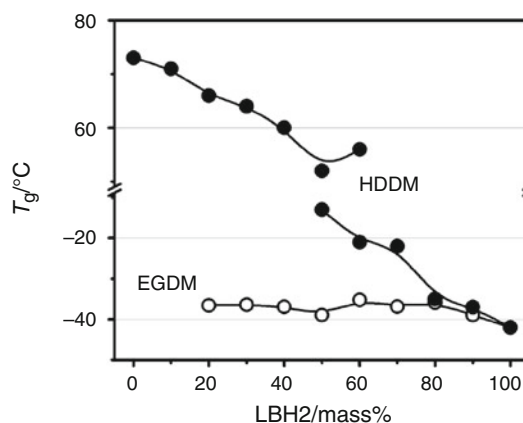
Fig. 2 Glass transition temperatures of semi-IPNs as a function of LBH2 content

concentration. In the case of polyEGDM-based IPNs we observe only one T_g corresponding to LBH2 phase, which is practically independent of the LBH content up to about 70 mass%. This T_g is slightly shifted to higher temperatures in comparison to the neat LBH2 ($T_g = -42$ °C) indicating incomplete phase separation. The fact that it is very close to the T_g of the neat LBH2 means that the LBH2 glass transition is barely influenced by polyEGDM network formation. This suggests in turn that there is no restriction of segmental motion of LBH2's chains by polyEGDM (being in glassy state at LBH2 glass transition), which corresponds to situation when two polymers form separate domains and degree of mixing is small [5]. At LBH2 content >80 mass% the T_g behavior is dominated by LBH2 phase. The glass transitions of polyEGDM phase could not be observed in DSC curves what is a general rule in the case of dense polymer networks.

In the case of polyHDDM/LBH2 semi-IPNs the miscibility of the two polymers is much better, which can be concluded from T_g behavior of the semi-IPNs when changing the component ratio. Pure polyHDDM has the glass transition at 73 °C, but its T_g in the semi-IPNs is significantly shifted to lower temperatures with the
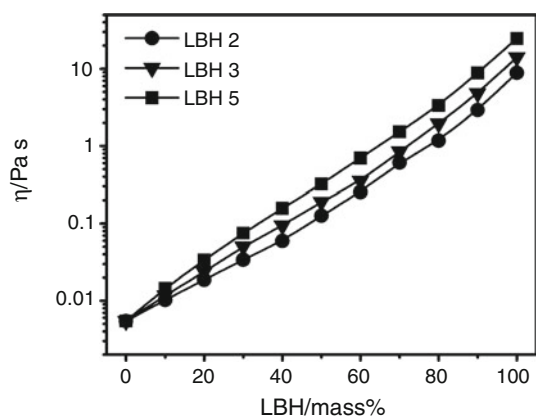
Fig. 3 Viscosity η of HDDM/LBH mixtures at 25 °C as a function of polybutadiene concentration and molecular mass

increasing LBH2 content. On the other hand, T_g of LBH2 shifts to higher temperatures with increasing polyHDDM content. This indicates on the existence of two phases: polyHDDM-enriched phase containing increasing amounts of LBH2 mixed with polyHDDM at the molecular level and LBH2-enriched phase containing polyHDDM. However, T_g of the latter for compositions containing up to about 50 mass% of LBH2 content in the IPN could not be observed due to too small amount of this separated phase. At 50 and 60 mass% of LBH2 content two T_g values appear showing clearly the existence of the above mentioned two phases. Further increase in LBH2/polyHDDM ratio leads to only one glass transition. This result can be interpreted as (i) the amount of polyHDDM-enriched phase was too small to influence the DSC curve or (ii) no phase separation occurred. The latter situation is possible when the process of separation is stopped by permanent entanglement of the chains [5].

Poorer compatibility of EGDM than HDDM with polybutadienesis also reflected in the values of solubility parameters EGDM 18.2 [28], 18.7 [29], HDDM 18.0 [29, 30], and polybutadiene 17.1 [30].

Photopolymerization kinetics

Viscosity

The dimethacrylate monomers used in this study have low and similar viscosities in 25 °C η of HDDM is 0.0055 Pa s and of EGDM 0.003 Pa s. On the other hand, the viscosities of liquid polybutadienes are much higher in 25 °C they are 8.87, 14.09, and 24.76 Pa s for LBH2, LBH3, and LBH5, respectively. Thus, the viscosities of monomer/polybutadiene mixtures increase significantly with the LBH content as shown in Fig. 3. The range of viscosities of the investigated formulations is very wide and covers four
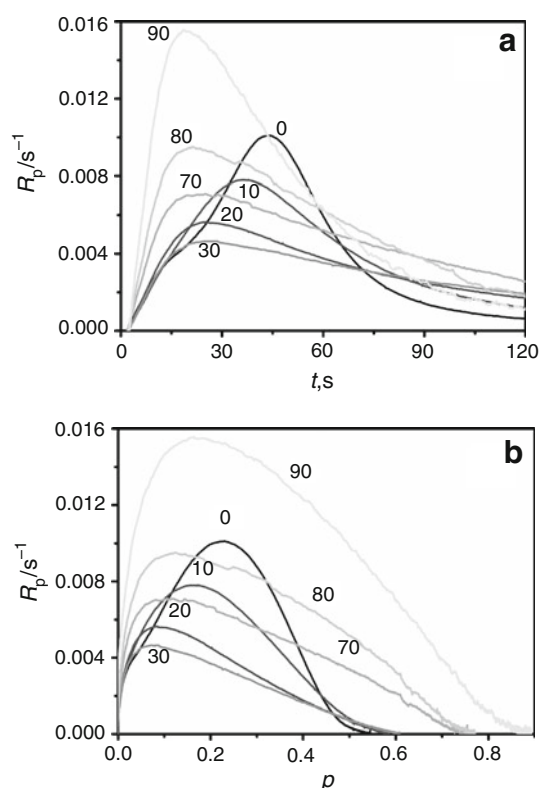

Fig. 4 Rate of polymerization R_p as a function of **a** irradiation time t, **b** double bond conversion p for HDDM/LBH3 system; the *numbers* indicate the LBH3 content (mass%) in the feed; polymerization temperature 25 °C

orders of magnitude (10^{-3}–10 Pa s), which, as will be shown, influences the photocuring kinetics.

Influence of polybutadiene molecular mass and concentration

The polymerization rates and conversions presented in Figs. 4, 5, 6, 7, 8, and 9 are referred to methacrylic double bonds without considering the double bonds from LBH. As mentioned above, the copolymerization of allylic monomers with methacrylates is limited. Although there are reports that polybutadienes may somewhat copolymerize with methacrylates [1, 31] this copolymerization is not taken into account in kinetic analysis [31]. Moreover, under our experimental conditions the LBH homopolymerization does not occur (no reaction heat is observed during photo-DSC measurements). However, we cannot completely exclude the copolymerization, especially at low LBH concentration [26, 27], and for this reason our results indicate trends rather than the actual parameters of the reaction.

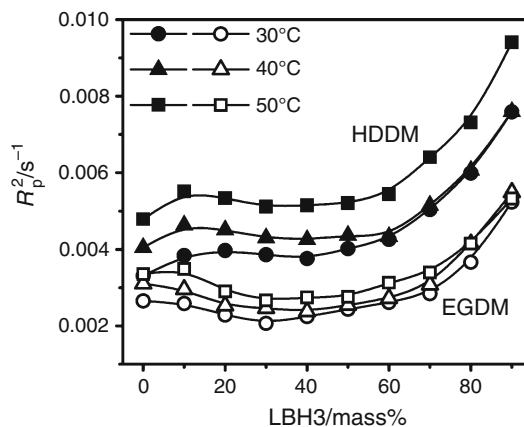Figure 4 presents the exemplary dependences of the polymerization rate (R_p) on irradiation time (t) and double
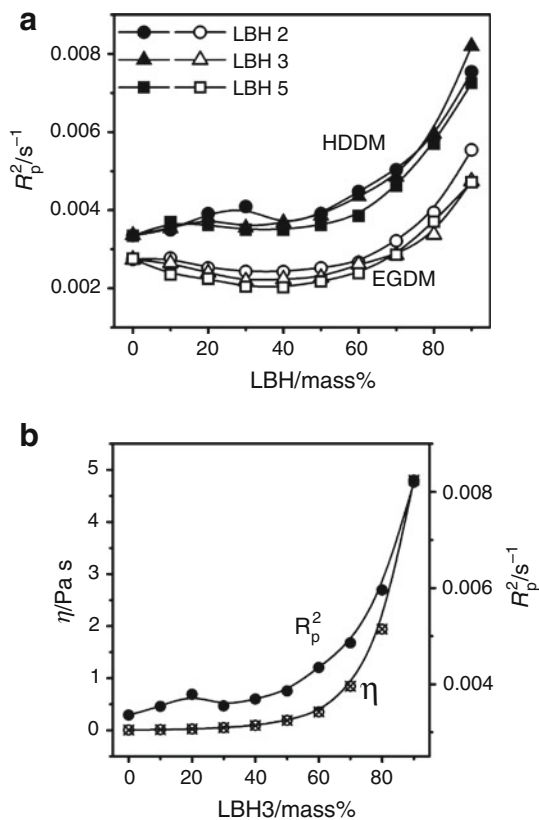
Fig. 5 a Rate of polymerization at 2 % of double bond conversion $R_p^{(2)}$ versus LBH content for HDDM/LBH and EGDM/LBH systems **b** initial viscosity and $R_p^{(2)}$ of HDDM/LBH3 system versus LBH3 content; polymerization temperature 25 °C
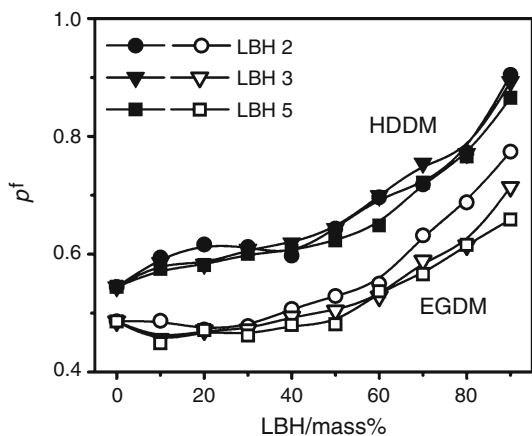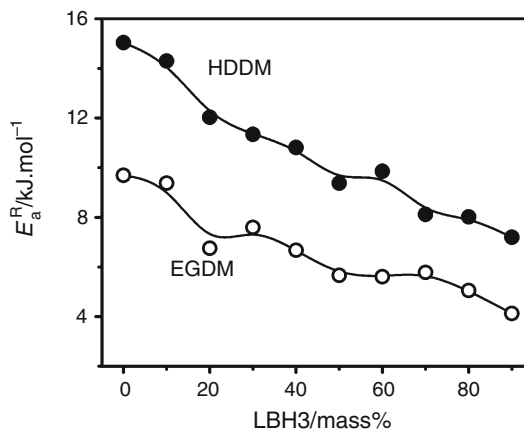

Fig. 6 Final double bond conversion, p^f as a function of polybutadiene content and polybutadiene molecular mass for HDDM/LBH and EGDM/LBH systems
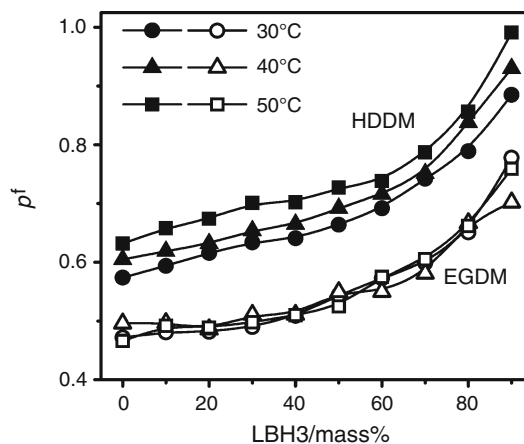

Fig. 7 Rate of polymerization at 2 % of double bond conversion $R_p^{(2)}$ versus LBH content at three different polymerization temperatures

Fig. 8 Activation energy for the polymerization rate at 2 % of double bond conversion

Fig. 9 Final double bond conversion p^f as a function of LBH3 content and polymerization temperature for HDDM/LBH and EGDM/LBH systems

bond conversion (p) for the photopolymerization of the HDDM/LBH3 mixtures at 25 °C. Kinetic curves obtained for other dimethacrylate/LBH systems behave similarly. The DSC traces registered for the neat HDDM have a bimodal shape typical for the polymerization of a

multifunctional monomer of low viscosity [14]. The $R_p = f(p)$ curve shows a slight inflection point at about 4–5 % of double bond conversion, which corresponds to

the beginning of autoacceleration. At about 23 % of double bond conversion the polymerization rate reaches its maximum value, R_p^{max} associated with the end of the gel effect.

As LBH3 is added R_p^{max} decreases and when the polybutadiene content reaches 30 mass%, the autoacceleration is supressed due to the increase in mobility of macroradicals as a result of dilution and plasticisation of the system; the efficiency of radical termination becomes nearly the same throughout the entire polymerization [32]. On the other hand, the rate of polymerization on the shoulder of the curve, prior to autoacceleration, increases with increasing concentrations of LBH. This is a consequence of the increased initial viscosity of the system and resulting enhanced diffusional limitations of the termination process in classical kinetics the termination rate coefficient k_t^b is inversely proportional to the viscosity ($k_t^b \sim 1/\eta$), and the polymerization rate R_p is related to the termination rate coefficient as $R_p \sim 1/(k_t^b)^{0.5}$. The rates of polymerization at 2 % of double bond conversion ($R_p^{(2)}$) versus LBH content are shown in Fig. 5a.

In the case of HDDM/LBH systems, a slight increase of the polymerization rate $R_p^{(2)}$ is observed up to about 50 mass% of LBH content. Further, increase in LBH concentration results in a rapid acceleration of the polymerization. This behavior correlates qualitatively well with changes of initial viscosity during increasing LBH content (Fig. 5b). However, a quantitative correlation of these parameters cannot be found due to the influence of additional parameters on the polymerization rate. In general, the polymerization rates of EGDM/LBH systems are lower than these of HDDM/LBH systems due to the formation of denser polymethacrylate networks [33]. In this case, even a slight decrease in $R_p^{(2)}$ is observed before the rapid growth of the rate at higher LBH contents. This may point to a retardation of the polymerization, which is better observable in the concentration range where the increase in viscosity is not large (LBH content 0–50 mass%). The retardation can result from a partial copolymerization with LBH in nonseparated domains and extensive chain transfer with the formation of allyl-type radicals of very low reactivity (degradative chain transfer) [22]. The chain transfer from the propagating methacrylate radicals to polybutadiene is less probable due to lowered reactivity of these radicals toward chain transfer and enhanced reactivity toward propagation [22].

However, very high initial viscosity of the investigated systems affects also the propagation rate, which can be concluded from the reduction of the polymerization rate when LBH molecular mass is increased. In our case, such reduction is not high due to rather small differences between viscosities of the investigated systems. Under such conditions diffusional limitations on propagation begin to occur at increasingly smaller conversions; this leads to a reduction of the polymerization rate. The observable influence of viscosity on $R_p^{(2)}$ points to the lack of phase separation at low conversions. Separation appears when the polymethacrylate chains reach a suitable length. The viscosity effects are less pronounced in EGDM/LBH systems due to poorer compatibility between the polyEGDM network and LBH.

As long as the visible phase separation is observed, the final double bond conversion p^f practically does not depend on LBH contents (for polyEGDM) or depends only slightly (for polyHDDM), as can be seen from Fig. 6. The lack of this dependence observed in the first case suggests that the EGDM polymerization occurs in the separated phase (despite the initial full miscibility of the components). When polymerized material becomes visually homogeneous, p^f starts to increase with LBH content indicating in turn that the polydimethacrylate network swollen by polybutadiene has greater mobility, which enables higher conversion of double bonds. Better compatibility of polyHDDM with LBH causes that p^f slightly increases even in the presence of small amounts of LBH, and the phase separation is partial. These results are supported by T_g behavior. However, as mentioned above, we cannot completely exclude LBH (co)polymerization.

Effect of temperature

The polymerization kinetics was followed at 25, 30, 40, and 50 °C. The $R_p^{(2)}$ values registered at 30, 40, and 50 °C are shown in Fig. 7 as a function of LBH3 content.

As could be expected, the polymerization rate increases with temperature, but stronger for HDDM-based systems. This indicates that the activation energy for the polymerization rate E_a^R is higher for these systems, which is illustrated in Fig. 8 showing this parameter calculated for the reaction rate at 2 % of conversion.

In the case of photochemical initiation, E_a^R is expressed by the following equation:

$$E_a^R = E_a^p - 0.5 \cdot E_a^t, \tag{1}$$

where E_a^p denotes the activation energy for propagation, and E_a^t is the activation energy for termination (activation energy of initiation is close to zero). Lower E_a^R values for EGDM-based systems can result from higher E_a^t of EGDM polymerization due to formation of denser polymer network hindering movements of radical ends. On the other hand, activation energy for termination corresponds to temperature dependence of inverse viscosity of the system [34]. Such dependence is usually high for viscous monomers and resins. Thus, the decrease of E_a^R with increasing LBH content results mainly from an increase in E_a^t in Eq. (1).
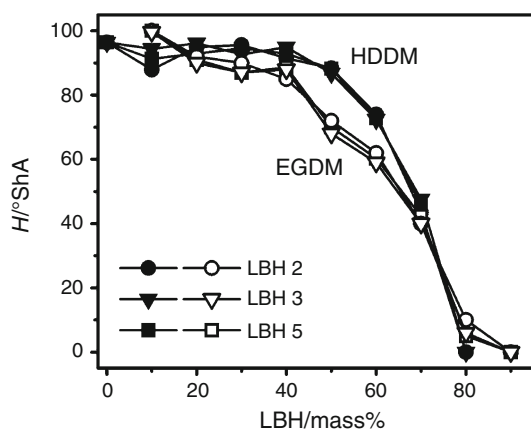
Fig. 10 Shore A hardness H as a function of polybutadiene content

The increase in the polymerization temperature results in enhanced phase separation. Instability of the system is driven by the progressive increase of the average molecular mass of the polymerizing species; the degree of demixing depends on the competition between phase separation dynamics and reaction kinetics. Due to rapid decrease of viscosity with increasing temperature, diffusion of polymer chains from each other becomes easier, which facilitates the phase separation.

The increase in polymerization temperature causes also an increase in the final conversion degree (Fig. 9). At higher temperatures the mobility of reacting species increases allowing the system to react for a longer time and reach higher conversions. In the case of EGDM-containing systems the temperature affects the conversion only slightly, which can be related, i.e., to the slight effect of temperature on the polymerization rate.

Hardness testing

The obtained semi-IPN materials were tested for their Shore A hardness. The results are shown in Fig. 10. Interestingly, the hardness remains practically constant for HDDM-based systems up to LBH content 40 mass% and rapidly drops at higher LBH addition. For the EGDM-based systems the hardness decreases slightly with increasing LBH content and similarly as in the previous case, rapidly decreases when LBH content exceeds 40 mass%. Generally, it is lower for polyHDDM-containing semi-IPNs. It is against expectation that EGDM-based materials will be harder due to more dense methacrylate network. The observed higher hardness of materials with polyHDDM matrix can result from higher double bond conversion leading to higher crosslink density (Fig. 8).

The observed behavior of the hardness with increasing LBH content can be explained by phase separation observed in the materials containing up to about 50 mass% of the linear polymer. Such a physical structure results in toughening of the glassy polymer matrix, because the LBH dispersion facilitates shear yielding of the matrix and hence cracktip blunting [12]. This may be the reason of the practically constant blend hardness to the LBH content of about 30–50 mass% (especially in the case of HDDM/LBH systems). Better compatibility of the polymeric components in this semi-IPN results in better adhesion at their interphase which positively influences mechanical properties. Above this LBH level the two polymer phases become compatible, and LBH begin to act as a plasticizer causing stepwise decrease of hardness.

Conclusions

Partly miscible polymer blends of polyHDDM and poly-EGDM with LBHs of various lengths were obtained in the form of semi-IPNs. In the case of polyHDDM-containing semi-IPNs the miscibility of the two polymers is much better, which can be concluded from semi-IPN's T_g behavior. The extent of phase separation depends on LBH content; materials containing LBH in amounts exceeding 50 mass% become optically homogeneous.

Addition of LBH to the monomers results in suppression of the gel effect; the polymerization rate at low conversions does not depend on LBH content up to about 50 mass%, but rapidly increases at higher contents, which is associated with the disappearance of the phase separation and the resulting increase in the viscosity of the polymerizing medium.

The phase separation affects hardness of the materials. The hardness remains practically constant (polyHDDM matrix) or changes only slightly (polyEGDM matrix) when the phase separation takes place, but when the blends become homogeneous the hardness rapidly decreases due to plasticization of the material by LBH.

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