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GRAFTING AND DEGRADATION REACTIONS AT THE SYNTHESIS OF INTERPENETRATING POLYMER NETWORKS IN SITU FROM POLYETHYLENE AND BUTYL METHACRYLATE

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ABSTRACT

The grafting and degradation reactions accompanying the synthesis of interpenetrating polymer networks (IPN) in situ consisting of polyethylene (PE) and poly(butyl methacrylate) (PBMA) were investigated under model conditions. After polymerization at 110°C it was found that the 2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexane (Luperox-101) had a destructive effect on the PBMA network formed provided the temperature was raised to 160°C. Simultaneously in this reaction stage, further linkage of the PBMA chains with PE originates from a recombination of macroradicals from both polymers. In the thermally initiated polymerization of BMA (in the absence of peroxide), PE is grafted with BMA but no crosslinking of PE takes place. If a mixture of initiators (2,2′-azo-bis-isobutyronitrile and Luperox-101) was used, a retardation of PE grafting with BMA was observed. A considerable degree of PE crosslinking and grafting of PBMA onto a PE network was achieved if both polymers were mixed with 3 mass % of Luperox-101.

INTRODUCTION

In preceding investigations some IPN-like systems were prepared by using the synthesis in situ [1, 2]. The principle of the method consists in dissolution of PE as a component in vinyl monomer or in a mixture of two monomers at increased temperature. In the synthesis of this IPN system, first BMA polymerizes in the presence of polyfunctional monomer and subsequently polyethylene is crosslinked by the effect of a peroxidic initiator. Because of the radical character of the reactions mentioned, a great number of side reactions is presumed, the extent of these reactions under the conditions of preparation of the IPN system PE–BMA [1] is a topic of this paper. As a matter of fact, we can expect that no ideal IPN system, the major characteristic of which is independence of two polymer networks without chemical bonding [3–5], comes into existence. One may assume that covalent bonds are formed between chains of independent networks (therefore, IPN-like systems). We can class the transfer reactions of radicals of initiator and polymethacrylate macroradicals to polyethylene as such side reactions. The polyethylene macroradicals generated are able to react with the monomers present and grafting of polyethylene starts. The formation of graft copolymers in the synthesis of IPN was assumed in previous papers [6, 7]; however, quantitative experiments to ascertain these processes has been rare.

We can suppose that the alkoxy radicals attack not only polyethylene but also polymethacrylate chains in the second step of crosslinking of polyethylene chains. The existence of the macroradicals thus formed results in the formation of crosslinked polyethylene, partial degradation of polymethacrylate chains, as well as in the mutual recombination reaction between polyethylene and poly(butyl methacrylate) radicals. However, this type of side reaction also gives rise to chemical bonds between components of both independent networks.

From the viewpoint of phase morphology of IPN, the system must be heterogeneous according to previous papers [1, 2]. The parallel process of grafting can improve the compatibility of components of the polymer system, and thus the problem of finding the optimum procedure for the synthesis of IPN could be interesting.

A polyfunctional monomer cannot be used for quantitative estimation of transfer side reactions in the first step because of crosslinking.

EXPERIMENTAL

Materials

Polyethylene (PE) of the low density (Bralen RA 2-19 type) was used in powder form, with a melt flowing index 1.7–2.3 g/10 min (product of Slovnaft, Bratislava).

Butyl methacrylate (BMA), a 99% product of Merck-Schuchard, was deprived of stabilizer by shaking with a 5% solution of NaOH as described in the literature [8] and distilled under reduced pressure before use.

Initiators

Luperox-101 (DTBPH), 2,5-dimethyl-2,5-di-(*t*-butylperoxy)-hexane, 90%, a product of Pennwalt-Wallace & Tierman-Chemie GmbH, was used without any purification.

2,2′-Azo-bis-isobutyronitrile (AIBN), a product of Serva, was crystallized from dried ethanol before use.

Solvents for Extraction

Methyl ethyl ketone, xylene, and methanol were products of Lachema, Brno; they were used without any purification.

Polymerization Procedure

The polymerization was carried out in two ways.

(a) Polymerization in Glass Ampule. About 1 g PE, the corresponding amount of butyl methacrylate, and the corresponding amount of peroxide were put in a narrow neck ampule. This ampule was sealed in nitrogen atmosphere. The reaction was allowed to proceed at the necessary temperature in an oil bath.

(b) Polymerization between Two Glass Plates. Polyethylene was dissolved in butyl methacrylate in nitrogen atmosphere at an elevated temperature (110°C). After dissolution of PE the necessary quantity of initiator (Luperox-101) was added and the PE solution was poured between two glass plates which were sealed with PVC tubing and heated to the reaction temperature. The mold was put into a drier where the polymerization proceeded in nitrogen atmosphere at 110°C for 6 hours. Finally, the sample was exposed to a reaction temperature of 160°C for 1 hour.

Extraction

The nonconsumed monomer and the low-molecular products which might originate in destruction reactions through the effect of peroxide were extracted with methanol. The homopolymer of butyl methacrylate was extracted from the polymerized mixture with methyl ethyl ketone. The selectivity of methanol and methyl ethyl ketone extraction was verified by gas chromatography and mass spectroscopy after pyrolysis of the extracted polymer. Pyrolysis gas chromatography was carried out by means of a pyrolyzer Pyroprobe 2000 (CDS Instruments) coupled with a gas chromatograph 5890 (Hewlett-Packard) with mass selective detector 5971A. The pyrolysis temperature was 700°C. The noncrosslinked PE or PE grafted with BMA was extracted with xylene. The insoluble residue was regarded as the crosslinked product, the composition of which was calculated from the overall balance of extracts. All extractions were carried out at the boiling point of the solvent used.

Working Procedure. About 1-2 g polymerized sample was weighed in a closed bag of glass fibers and extracted with a 50-fold amount of solvent in a flask equipped with a reflux to which the nitrogen inlet was attached. The extraction was accomplished at the boiling point of solvent and took 20 hours for xylene, 20 hours for methyl ketone, and 6 hours for methanol. The solvent was replaced three times in the course of extraction.

After extraction the sample was rinsed with pure solvent and dried in a vacuum drier at 110°C for 8 hours.

Selective extraction was used for the successive separation of individual products of polymerization, i.e., homopolymer, grafted polymer, and polymer network.

RESULTS AND DISCUSSION

Grafting and Crosslinking of PE with BMA by the Effect of Peroxide

The influence of Luperox-101 concentration on the grafting and crosslinking process was investigated in the first series of experiments performed at a constant molar ratio of [PE]:[BMA] = 1 (16.4 mass % PE) and 110°C (Table 1). In this series of experiments we also investigated the influence of PE crosslinking on the formation of crosslinked copolymer with the reaction temperature increased to 160°C.

It follows from the results of methanol extraction that 6 hours of polymerization of butyl methacrylate leads to full conversion of monomer in the PE matrix over the entire concentration range of peroxide. Polymerization is evidently accelerated by the gel effect which is favored by the dissolved PE from the beginning of the reaction. The increase in peroxide concentration gradually raises the fraction of components soluble in methanol of the system (peroxide, soluble oligomers, and decomposition products of polymers). The subsequent increase in temperature (for 1 hour) of the polymer reaction mixture to 160°C increases the solubility of the sample in methanol, which indicates a partial degradation of poly(butyl methacrylate) by alkoxy radicals originating from peroxide decomposition. The difference in methanol solubility of the samples annealed at 110 and 160°C related to the amount of decomposed peroxide systematically increases with a decrease of peroxide concentration, which could be a manifestation of the competition between monomolecular chain fragmentation reactions and bimolecular termination reactions. That is, owing to increasing radical concentration in the system, the rate of termination increases with the square of the peroxide concentration while the rate of fragmentation increases only linearly. Therefore, an increase of peroxide concentration brings about a decrease in the relative share of the chain fragmentation reaction initiated by the decomposition of peroxide. A similar destructive influence in the subsequent step on the results of the preceding reaction in IPN synthesis has been observed for other systems [9].

The percentage of the rest of the samples polymerized at 110°C which are insoluble in methyl ethyl ketone shows that the grafting efficiency of butyl methacrylate on polyethylene is proportional to the peroxide concentration raised to the 0.38th power (Fig. 1). The exponent was calculated by the method of least squares as the slope of the logarithmic relation, the correlation coefficient being 0.994. The reduced value of exponent with respect to a value of 0.5, which could be expected,

TABLE 1. Mass Percentage of Insoluble Residue of Crosslinked PE Grafted with BMA in Boiling Solvents [methanol (MeOH), methyl ethyl ketone (MEK), and xylene (XYL)] after 6 Hours' Polymerization at 110°C and Subsequent Annealing of a Parallel Sample for 1 Hour at 160°C. The Starting Mixture in BMA Contained 16.4 mass % of PE; Polymerizations Were Carried Out in Glass Ampules

		Percent of insoluble residue for extraction time (in hours) of		
Peroxide, mass %	Temperature, °C	6, MeOH	20, MEK	20, XYL
0.05	110	98.0	19.3	0
	160	96.7	19.6	0
0.5	110	97.6	22.3	0
	160	95.3	22.3	0
1.0	110	97.0	24.8	0
	160	94.8	24.3	11.0
1.5	110	96.9	26.8	0
	160	94.0	26.6	18.1
2.0	110	96.3	27.9	0
	160	93.4	29.0	22.4
2.5	110	96.2	29.0	0
	160	93.8	34.0	28.9
3.0	110	95.9	28.8	0
	160	92.5	44.0	36.5

indicates the primary termination of macroradicals or their transfer reaction with the present peroxidic initiator. These results do not allow us to determine whether only the more reactive alkoxy radicals or also the propagating butyl methacrylate radicals are responsible for polyethylene grafting.

In the first stage of IPN synthesis the formation of crosslinked polyethylene (recombination of grafted branches) cannot be observed, although a rather large portion of grafted polymer is created. This can be explained by the large amount of transfer reactions of growth radicals as well as by the fact that disproportionation is the main result of the termination reaction of the propagating butyl methacrylate radicals.

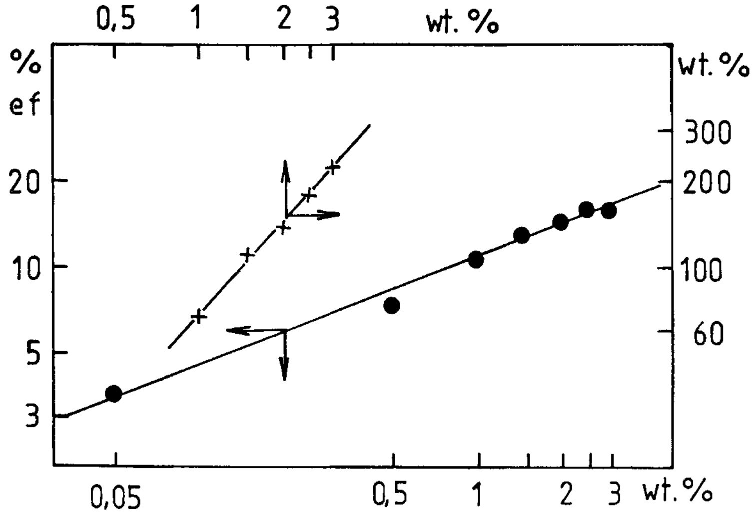

FIG. 1. Logarithm of the percentage of bonded BMA on PE (grafting efficiency: *ef*) found at polymerization at 110°C (filled circles). Logarithm of the percentage of the grafted BMA on crosslinked PE at 160°C (related to original amount of PE) (crosses) as a function of DTBPH concentration. Molar ratio of PE/BMA = 1.

In the second stage of IPN preparation (1 hour annealing of samples at 160°C), the formed poly(butyl methacrylate) is liable to bond further with polyethylene. The bonding of PBMA with PE is a result of the recombination of macroradicals of both polymers originating in the transfer reactions of alkoxy radicals descending from peroxide to polymer.

The results of xylene extraction confirm the bonding of PBMA on the PE network, while the amount of grafted PE with PBMA for the highest concentration of peroxide is greater than the original PE content alone (Fig. 1). The amount of crosslinked product is proportional to the concentration of peroxide [—O—O—] in this case. (The calculated exponent n in the expression gel % = $K[\text{—O—O—}]^n$ is equal to 1.06, the coefficient of correlation being 0.997.)

Grafting and Crosslinking of PE with BMA in the Absence of Peroxide

In order to distinguish the effect of alkoxy radicals from the effect of PBMA growth macroradicals in the initiation of PE grafting, we performed thermal polymerization without any initiator (Table 2). The question is: How much is the degree of PE grafting with BMA affected if the reaction starts on PE? That is, the PE macroradicals as nuclei of grafting are formed only by transfer of the PBMA growth radicals to PE and not by the effect of alkoxy radicals originating from the peroxide. The results of extraction show that grafting proceeds even under these conditions. Its efficiency is more affected by the change in PE concentration than by temperature within the 110 to 170°C range. If we consider the activation energy of the transfer reaction of macroradical to PE (which is, in general, higher than the activation energy of the addition reaction of monomer to macroradical), then an

TABLE 2. Mass Percentage of BMA Grafted on PE Related to Total Amount of Monomer Polymerized for 6 Hours at Different Temperatures and PE/BMA Ratios. The Data Have Been Calculated from the Insoluble Fraction in Boiling Methyl Ethyl Ketone; Extraction Took 20 Hours

Molar ratio PE/BMA	Mass % of PE	Efficiency of grafting (%) at 110°C	120°C	140°C	170°C	Slope[a] a_2
1	16.4	5.6	10.2	8.9	18.1 (8.6)[b]	0.18
2	28.2	38.3	26.1	32.1	29.0 (3.7)[b]	−0.08
3	37.0	59.1	38.4	23.8	33.2 (1.0)[b]	−0.37
4	43.9	54.0	39.4	24.4	32.1 (0.7)[b]	−0.33
5	49.5	46.9	46.5	40.2	33.3 (0.2)[b]	−0.24
Slope a_1		9.8	8.6	5.5	3.4	

[a] Slopes of the plot of molar ratio (a_1) or temperature (a_2) versus grafting efficiency were calculated by the method of least squares on the assumption of a linear relationship.

[b] Values in parentheses correspond to the percentage of the amount of cross-linked grafted polymer and PE; the fraction insoluble in methyl ethyl ketone corresponds to 100%.

increase in temperature ought to favor the transfer reaction and thus raise the efficiency of grafting. However, for the majority of samples (Table 2), an increase in temperature reduces rather than enhances the efficiency of grafting (negative slope).

In order to clarify the complicated influence of variables on the efficiency of grafting, we can use a series of kinetic equations. The instantaneous efficiency of monomer grafting on PE (*ef*) can be expressed by the ratio of the rate of grafting to the overall rate of butyl methacrylate consumption:

$$ef = \frac{k[\mathrm{PE}^{\cdot}][\mathrm{BMA}]}{k[\mathrm{PE}^{\cdot} + \mathrm{PBMA}^{\cdot}][\mathrm{BMA}]} = \frac{1}{1 + [\mathrm{PBMA}^{\cdot}]/[\mathrm{PE}^{\cdot}]}$$

In a stationary state the rate of formation of all radicals is equal to the rate of decay of these radicals:

$$v_i = k_3[\mathrm{PE}^{\cdot} + \mathrm{PBMA}^{\cdot}]^2$$

In addition, the rate of formation of PE macroradicals in a stationary state is equal to the rate of their decay:

$$k_4[\mathrm{PBMA}^{\cdot}][\mathrm{PE}] = k_3[\mathrm{PBMA}^{\cdot}][\mathrm{PE}^{\cdot}] + k_3[\mathrm{PE}^{\cdot}]^2$$

The symbols v_i, k_3, and k_4 represent the rate of initiation, the rate constant of termination, and the rate constant of transfer of hydrogen atoms of PE to PBMA radicals, respectively. Thus, for the concentration ratio of both macroradicals:

$$\frac{[\mathrm{PBMA}^{\cdot}]}{[\mathrm{PE}^{\cdot}]} = \frac{k_3^{0.5} v_i^{0.5}}{k_4[\mathrm{PE}]}$$

According to this relationship, a decrease in grafting efficiency due to increasing temperature is to be expected in the case where the activation energies of the mentioned reactions obey the following relationship:

$$0.5(E_3 + E_i) > E_4$$

This situation comes into existence if the influence of the gel effect prevails in the process of grafting. Therefore, it seems reasonable that the decrease in grafting efficiency due to increasing temperature is greater for higher PE/BMA ratios (a similar interpretation is appropriate for the decreasing slope a_1 with increasing temperature) (Table 2).

The determination of the insoluble residue in boiling xylene has shown that almost all samples were completely soluble. Partial insolubility was manifested only by those samples that had been grafted at the highest temperature. We may state that the grafting accomplished even at 170°C represents only a small part of the reaction components.

Grafting and Crosslinking of PE in the Presence and in the Absence of Peroxide

In contrast to the preceding results (Table 1), we note relatively great scatter of the data on grafting efficiency (Table 2). The variation of efficiency for small differences in the starting conditions may be due to differences in oxygen removal from powdered polyethylene if there is no source of free radicals in the system which can overlap the influence of oxygen. In spite of this uncertainty, the set of results reveals the following paradox. The value of grafting efficiency extrapolated to zero concentration of peroxide in the system (Table 1) is significantly lower than the similar extrapolated as well as measured value for 110°C (Table 2). It follows from this inconsistency of results that the peroxide present not only serves as a source of free radicals but also as an active reagent with the alkyl growth radicals of PBMA. This possibility has already been implied by the relatively low exponent value in the relationship between grafting efficiency and initiator concentration.

Influence of the Mixture of Initiators AIBN and DTBPH on Grafting and Crosslinking of PE

In order to elucidate and demonstrate the influence of peroxide, we carried out a series of experiments in which we used AIBN as initiator. These polymerizations were accomplished at 80°C in the presence of the more thermostable peroxide, i.e., DTBPH, in the system (Table 3). To facilitate the investigations, we chose a PE/BMA molar ratio of 3. The evaluated results of sample extraction with methyl ethyl ketone after polymerization at 80°C (Fig. 2) show that the grafting efficiency unambiguously decreases with increasing concentration of the peroxide used. Thus, the reactive peroxidic precursor of radicals has two opposite functions: it is able to initiate as well as to retard the grafting of polymer.

In the second stage of reaction at 160°C (1 hour) the initiators present in the samples decompose and produce further reactions. The bonding of PBMA chains

TABLE 3. Insoluble Fraction of PE Grafted with BMA at a PE/BMA Molar Ratio of 3 (37 mass % of PE) and 80°C for 20 Hours in the Presence of AIBN (0.3 mass %) after 20 Hours' Extraction with Methyl Ethyl Ketone (MEK) and Xylene (XYL). The Insoluble Fraction of the Parallel Sample Was Subsequently Annealed for 1 Hour at 160°C in the Presence of Different Amounts of DTBPH in the Reaction System

Peroxide DTBPH, mass %	Temperature, °C	Percent of insoluble residue	
		MEK	XYL
0.05	80	49.3	0.1
	160	37.5	0.4
0.5	80	39.9	0
	160	37.8	1.4
1.0	80	38.9	0
	160	39.5	13.7
1.5	80	41.4	0
	160	42.0	23.8
2.0	80	39.5	0
	160	43.9	27.3
2.5	80	38.2	0
	160	46.9	31.8
3.0	80	35.1[a]	0
	160	56.9	44.3[b]

[a] A part of PE was dissolved as grafted copolymer.

[b] There are undoubtedly bonded PBMA chains in the network structure as well.

with PE as well as the crosslinking of PE increase. The decrease in grafting at a low concentration of peroxide may be interpreted as due to simultaneous course of fragmentation reactions of macroradicals and the occurrence of competing reactions that are dependent on the stationary concentration of radicals in the system.

Reactions between PE and PBMA in Mixture by the Effect of Peroxide

The increase in grafting efficiency in the second stage of the reaction of the polymerized samples of PBMA in the PE matrix introduces a new problem. It

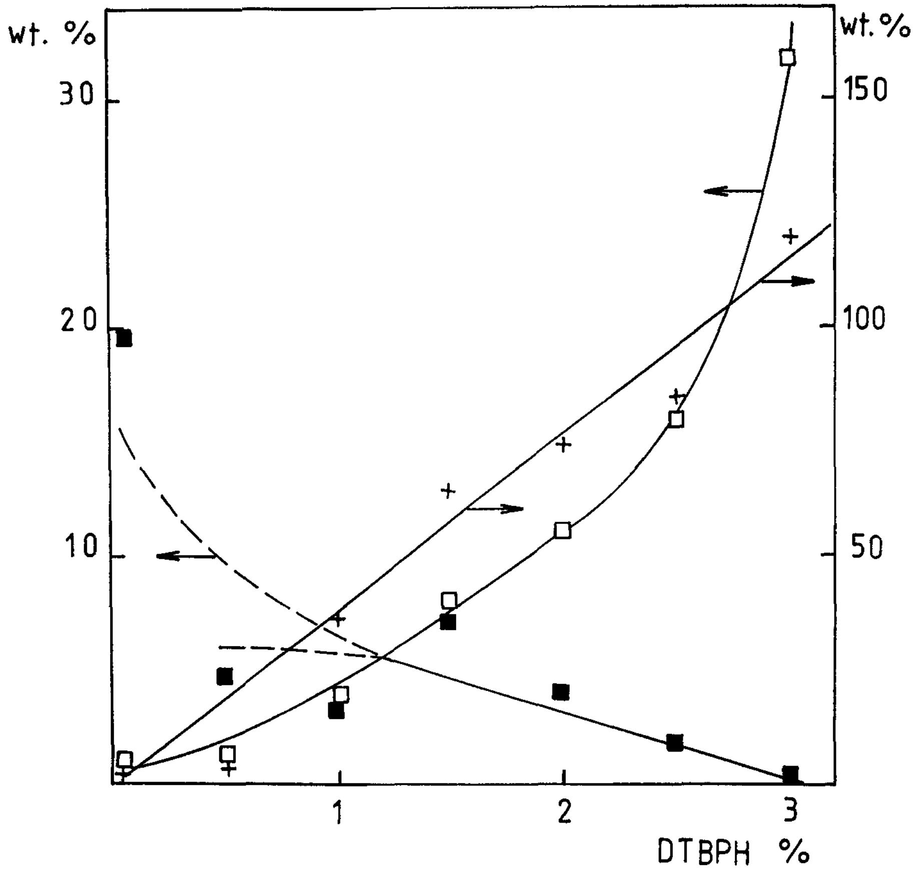

FIG. 2. Variation of the efficiency of BMA grafting on PE with DTBPH concentration. Polymerization of monomer was initiated by 0.3 mass % of AIBN at 80°C (20 hours) (filled squares) and subsequently the samples were annealed at 160°C (1 hour) (open squares). Crosses denote the gel content related to PE amount after final annealing of samples at 160°C. Molar ratio of PE/BMA = 3.

essentially consists of the question of whether the bonding of further chains to the grafted polymer is accompanied by a recombination of PBMA macroradicals or of PE radicals joining the PBMA radicals. In order to clear up this question, we performed a similar experiment in which we eliminated PE from the reactant system. After the polymerization of BMA at 80°C up to complete conversion, all samples were soluble in methyl ethyl ketone. After annealing the parallel samples at 160°C, the samples were constantly soluble in methyl ethyl ketone. A significant increase in methanol solubility occurred. On the basis of these results we may assume that the increase in grafting efficiency through the effect of DTBPH on the PE-PBMA mixture is due to recombination of unequal macroradicals from both polymers. In order to support this indirect evidence, we carried out an experiment in which we mixed the purified (precipitated) PBMA (prepared by polymerization of BMA with 0.05% AIBN at 60°C) with PE at a molar ratio of 1:1 (16.4 mol%

PE) and 3 mass % peroxide (DTBPH). The polymer was stirred in a Brabender at 110°C and then the mixture was allowed to react in a press at 160°C (1 hour). The insoluble residue was equal to 72% after methyl ethyl ketone extraction and to 66% after xylene extraction. The higher degree of a PBMA grafting on PE when compared with BMA polymerization in a PE matrix may be due to a higher molecular mass of the prepared PBMA and a higher content of macroradicals in the system. An additional contribution of free radicals came from the mechanochemical generation of these active particles in the course of polymer stirring.

Influence of the Method of IPN Preparation

By synthesizing IPN between glass plates (preparation of samples for measuring the properties of IPN) as described in the Experimental Section, we systematically obtained a much higher degree of grafting than in experiments performed with sealed ampules. On the basis of these experiments, the observed difference may be explained by the higher homogeneity of the system due to mechanical stirring of the reaction components immediately before the start of thermal polymerization and the likelihood of a higher temperature in the first reaction stage involving annealing of the sample in an air thermostat where the removal of polymerization heat must be slower.

A supplementary picture of the grafting reactions is given by experiments in which we first crosslinked PE (160°C, 1 hour) and afterwards thermally polymerized BMA in this matrix (Table 4). By the use of this procedure (denoted by "A" in Table 4), we achieved the highest efficiency of grafting of BMA on PE (67-91%). The high degree of grafting in crosslinked polyethylene can be explained by the longer lifetime and supplementary generation of macroradicals by a mechanism similar to omega (popcorn) polymerization [10]. The trapped macroradicals in swollen crosslinked polyethylene react with monomer, and the crosslinked structure becomes denser owing to the recombination of macroradicals. Crosslinked grafted copolymers already exist in the macrogel, and consequently the solubility of the microgel structures of the grafted copolymer linked by chemical bonds is restricted. Such a mechanism could also be responsible for the large insoluble fraction of grafted polymer in xylene, even at the low concentration of peroxide used for crosslinking PE. This idea allows us to explain the influence of peroxide concentration of the formation of different close networks as well as the radical splitting which accompanies the swelling with monomer in the process of grafting BMA on PE.

The quite different effect of peroxide manifests itself if the initiator is decomposed in PE in the presence of monomer BMA (procedure "B" in Table 4). The essential result of this method is a relatively high efficiency of grafting without any formation of macrogel structures (complete solubility in xylene).

The decomposition of initiator in the presence of a reactive monomer is likely complete, and the radicals arising from the initiator react with monomer as well as with the PBMA radicals formed. The preferential solubility of initiator in the monomer phase also plays a role (at least in the initial stage of heating). The competitive reactions of primary radicals with PE are less important and, for this reason, they do not produce any crosslinking of PE but only its grafting. An equal degree of grafting may be a consequence of following causes, while a lower concentration of

TABLE 4. Grafting of PE and the Formation of Crosslinked Copolymer with BMA with Different Kinds of Initiator (DTBPH) Decomposition (A and B)

	A:[a] Insoluble residue, %		B:[b] Insoluble residue, %	
DTBPH, mass %	MEK, 20 h	XYL, 20 h	MeOH 6 h	MEK 20 h
0.05	94.2	79.0	99.0	59.0
0.5	79.0	57.2	99.0	59.9
1.0	88.4	68.3	98.2	59.3
1.5	89.3	75.0	96.8	58.8
2.0	91.8	79.3	97.1	59.5
2.5	92.3	79.8	97.3	59.6
3.0	93.2	81.6	97.0	60.3

[a] PE samples containing corresponding amounts of peroxide were crosslinked at 160°C (1 hour), extracted with boiling methanol, and dried to constant mass. After cooling with liquid nitrogen, the polymer was crushed and BMA was added. The charge (37 mass % PE) was sealed in a test tube in a nitrogen atmosphere and annealed for 8 hours at 110°C.

[b] A charge of powdered PE and peroxide was weighed in a test tube and then BMA was added. The tube was sealed in a nitrogen atmosphere and heated for 1 hour at 160°C.

radicals in the polymerization system facilitates the formation of copolymer with longer PBMA branches. At higher concentrations of peroxide, copolymers with a greater number of shorter branches must be created.

CONCLUSIONS

If we consider the results obtained from the viewpoint of model studies and estimate the influence of the crosslinking agent (polyfunctional comonomer), we must assume that the formation of IPN is accompanied by a further increase in linkage between the acrylate and polyethylene networks because of the reactivity of nonconsumed double bonds in addition reactions of macroradicals. Thus, in the PE-PBMA system the network structures are chemically bonded. The first binding of network structures occurs in the course of preparing the acrylate network by the use of competitive grafting on polyethylene. In the second stage, which involves the crosslinking of partially grafted polyethylene, the recombination of PE radicals with the network structure takes place, and so the number of chemical bonds between both types of polymers increases. From this point of view we cannot assume the existence of an IPN with two independent, continuous network structures for the pair of polymers investigated.

On the other hand, the grafting of polyethylene increases the compatibility of both polymers, and thus we can achieve better homogeneity, especially at the interface of two incompatible and mutually crosslinked polymers.

REFERENCES

[1] E. Borsig, J. Hrouz, A. Fiedlerová, and M. Ilavský, *J. Macromol. Sci.—Chem., A27,* 1613 (1990).

[2] E. Borsig, A. Fiedlerová, K. G. Häusler, R. M. Sambatra, and G. H. Michler, *Polymer, 34,* 4787 (1993).

[3] L. H. Sperling, ***Interpenetrating Polymer Network and Related Materials,*** Plenum, New York, 1981.

[4] D. Klempner and K. C. Frisch, "Interpenetrating Polymer Networks Based on Crystalline Polymers Deformed in Liquid Monomers," in *Advances in Interpenetrating Polymer Networks,* Vol. 3, Technomic Publishing Co., Lancaster, 1991, p. 53.

[5] D. Klempner, *Angew. Chem. Int. Ed. Engl., 17,* 97 (1978).

[6] M. Bryjak and W. M. Trochimchuk, *Angew. Makromol. Chem., 116,* 221 (1983).

[7] R. Wicish and W. M. Trochimchuk, *J. Polym. Sci., Polym. Lett. Ed., 27,* 321 (1989).

[8] D. Braun, H. Cherdron, and W. Kern, *Praktikum der makromolekularen organischen Chemie,* Hütig Verlag, Heidelberg, 1979.

[9] D. J. Hourston and M. G. Huson, *J. Appl. Polym. Sci., 45,* 1753 (1992).

[10] G. H. Miller, D. Chock, and E. P. Chock, *J. Polym. Sci., Part A, 3,* 3353 (1965).

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