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MORPHOLOGY AND DEGRADATION BEHAVIOR OF IPN BASED ON POLYETHYLENE AND POLYMETHACRYLATE

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ABSTRACT

Thin IPN films composed of polyethylene and polymethacrylates were synthesized by the *in situ* method in a plate reactor. Low density polyethylene (PE), and methyl (MMA), ethyl (EMA), butyl (BMA), and dodecyl (DMA) methacrylates were used for the preparation of the polymethacrylate phase.

The crosslinking of PE both by electron beam and by peroxide was investigated in terms of gel content. The degradation behavior of individual polymethacrylates was studied in the immediate presence of polyethylene by a gravimetric method. All polymethacrylates degrade more than crosslink independent of the length of the aliphatic ester side groups. Surprisingly, a notable degradation of PE/poly(dodecyl methacrylate) by irradiation was also found, which is inconsistent with results reported for pure poly(dodecyl methacrylate).

Scanning electron microscope (SEM) was used to observe morphology changes in the irradiated samples. Pores of about 200 to 400 nm in diameter were observed on the surface and in the bulk

phase of irradiated IPN. Flux measurements showed that some irradiated samples were permeable to ethanol, indicating an open porous structure which may be relevant for membranes.

INTRODUCTION

The technique of interpenetrating polymer network (IPN) is, among other mixing methods, the unique way to get stable polymer mixtures whose components are repulsive, i.e., thermodynamically incompatible [1]. The stability comes from the covalent bonds among the polymer networks. However, almost all IPN still show a characteristic feature of phase separation [2]. Whether a polymeric material has a fabric, spherical or co-continuous two phase morphology is of paramount importance to its ultimate properties [3]. Therefore, any changes in morphology may result in changes in the properties.

Borsig *et al.* [4] reported an *in situ* synthesis method to obtain IPN of polyethylene with polystyrene. They used polyethylene powder as the first polymer and styrene both as monomer and as solvent for polyethylene. The styrene acted finally as the second polymer network after polymerization in the presence of a divinyl monomer. It was shown that the two interpenetrating polymer networks did not appear in a real IPN form because grafting reactions occurred between the network of polyethylene and the polystyrene network. This type of IPN was therefore referred to as IPN-like materials by the authors [4, 5]. Schulze *et al.* used the above mentioned *in situ* method to synthesize IPN from polyethylene powder and methacrylates. They found that the morphology of the IPN was strongly affected by the composition and by the synthesis conditions [5]. The phase domains ranged from several dozens to hundreds of nanometer.

Depending on their structures polymers degrade or crosslink under high energy irradiation. Polyethylene is a typical example that will crosslink when subjected to radiation [3], whereas poly(methyl methacrylate) is a well-known electronic positive resist (i.e. degrades under irradiation) [6]. In a system consisting of polyethylene and polymethacrylates the former acts as the crosslinking species under electron beam irradiation, while the latter is the degrading component.

We are interested in investigating this system where crosslinking and degradation happen concurrently when subjected to energetic radiation. By partly degrading the polymethacrylate phase it should be possible to obtain a porous material which might be used as membranes for the purpose of microfiltration or ultrafiltration according to the described morphology [5].

EXPERIMENTAL

Materials

Polyethylene (PE) was a low density product with a melt flowing index of 1.7-2.3 9/10 min. (Bralen RA 2-19 type) in powder form. Methacrylate monomers (Aldrich) were stripped of stabilizer by distillation or washing with aqueous sodium hydroxide. 2,5-Bis(t-butylperoxy)-2,5-dimethylhexane (Trigonox -101) was a product of AKZO.

Synthesis of IPN Thin Films

To a flask equipped with a reflux condenser and a magnetic stirrer and placed in an oil bath polyethylene powder and a methacrylate monomer or a mixture of methacrylates were added. The molar ratio of methacrylate monomer units to ethylene units was 1:1. Trigonox -101 was used as initiator. By increasing the temperature to 95°-105°C, a clear homogeneous solution of polyethylene in methacrylates was obtained. The polymerization reaction was performed *in situ* in a reactor which was composed of two PTFE plates and two metal plates and one PTFE frame of about 0.3 mm thick as spacer. The PTFE frame was located between the two PTFE plates which were fixed by the two metal plates. The reactor was preheated in an oven at 115°C. Trigonox-101 was added to the reaction solution and mixed with the stirrer shortly before the reaction solution was poured onto one PTFE plate. The reactor blocks were then fixed with parallel clams. The polymerization was carried out at 115°C for 6 hours and at 160°C for 1 hour. Table 1 shows the compositions of the reaction solution in which PE, DMA, BMA, EMA, MMA and BDDM stand for low density polyethylene, dodecyl methacrylate, butyl methacrylate, ethyl methacrylate, methyl methacrylate and butanediol dimethacrylate, respectively.

Methods

Electron Beam Irradiation

The irradiation was done by means of the electron beam accelerator EB ELV-2 (INP Nowosibirsk, Russia). The energy of accelerated electrons was 0.6 MeV. Samples were fixed with adhesive tapes on a metal plate. To avoid overheating and thus destroying the samples, an irradiation dose of 50 kGy or 100 kGy was used for individual irradiation. Higher doses were realized by multiple irradiation of samples.

Solvent Extraction

Extraction experiments were carried out in a round flask with about 100 times weight excess of the solvent at boiling. Methanol was selected to remove unreacted monomers and short chain molecules that may be formed by degradation during the irradiation. Xylene was used to extract linear or branched components, i.e. components which were not crosslinked in the networks. Finally, the samples were dried under vacuum at 50°C for 10 hours.

Electron Microscopy

The morphology was studied by a Zeiss scanning electron microscope (SEM) (DSM 982 GEMINI, Zeiss, Germany).

Flux Measurement

Permeability to ethanol was measured on a self-made apparatus with an effective diameter of 4 cm.

RESULTS AND DISCUSSION

Crosslinking of Polyethylene Under Irradiation

The most important application of electron beam radiation in industry is the crosslinking of polyethylene to produce insulating cables and other products [3].

In our experiments, polyethylene powder was hot pressed to thin films. The effect of electron beam irradiation on polyethylene was studied by determining the gel content of thin films after irradiation. While the unirradiated sample was completely dissolved in xylene, a gel content of 63.9% for the irradiated sample at 100 kGy was reached which increased with the irradiating dose (Figure 1). At an irradiation dose of 800 kGy, the gel content was 89.6%. Degradation of polyethylene to short chain molecules under irradiation was not observed. No weight loss could be determined in samples after irradiation and extraction with methanol.

The effect of peroxide on the crosslinking of polyethylene was also studied for comparison since Trigonox-101 was the initiator of the polymerization reaction. Two pieces of polyethylene thin film were dipped in pure Trigonox-101 for 72 hours and the sticking Trigonox-101 was then wiped off. The films were then subjected to the identical conditions as those for the preparation of IPN, i.e., they were thermally annealed for 6 hours at 115°C and 1 hour at 160°C. The remaining Trigonox-101 and its low molecular decomposed products were removed by extraction of the films with methanol. A gel content of 91.5% was found by

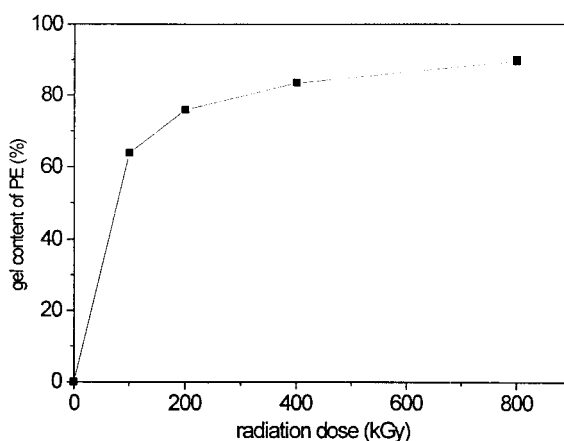


Figure 1. Dependence of the gel content of PE films on the radiation dose.

extraction with xylene. The other piece of film crosslinked by peroxide was additionally irradiated at 800 kGy, resulting in a gel content of 93.3%. A hot pressed PE film which was heated in the same manner was completely soluble in hot xylene, indicating that no thermal crosslinking occurred in this material.

According to the reference [3], the crosslinking of polyethylene under electron beam irradiation takes place mainly in the amorphous domains, i.e. in the noncrystalline regions. However, polyethylene crystallizes readily because of its molecular regularity. A weight increase of just 0.3% after dipping the polyethylene film in Trigonox for 72 hours indicates that the diffusion of peroxide molecules into the semicrystalline polyethylene is rather restricted. Nevertheless, both electron beam irradiation and peroxide yielded high gel contents. This may be attributed to the fact that the long chains of polyethylene molecules stretch from one crystalline district to another across amorphous regions. A few crosslinking units in amorphous domains are sufficient enough to form an insoluble network. Crosslinking by peroxide coupled by irradiation raised the gel content only by about 2%.

Dependence of Degradation of Polymethacrylates on Irradiation Dose

Most polymers degrade under irradiation [7] which is characterized by the decrease of their molecular weight. The estimation of the molecular weights is a popular method to get information about the degree of degradation.

M. Lazar *et al.* reported that methacrylates will be grafted onto polyethylene when they are polymerized in the presence of polyethylene [8]. Taking advantage of

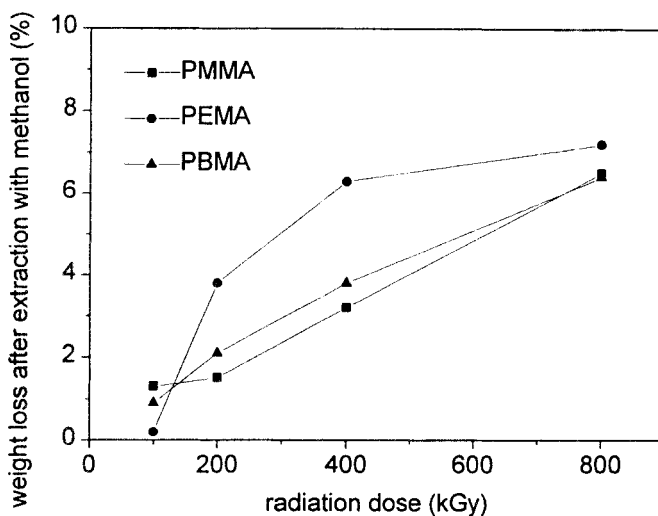


Figure 2. Dependence of degradation to short chain products on the radiation dose.

this, we introduce here a gravimetric method to investigate the degradation behavior of polymethacrylates which are grafted to a PE backbone. We assume it will fit better the situations in the materials investigated in our lab.

Thin films of PE which were first slightly crosslinked with 100 kGy and then extracted two times with xylene (10 hours each) at boiling heat to remove uncrosslinked moieties were used as framework. This network was swollen at 90°C for 2 hours in a solution of methacrylate monomer and Trigonox-101. The methacrylate monomer soaked into the polyethylene network was then polymerized under the same conditions as for the IPN preparation. The resulting films were extracted again with xylene to remove the polymethacrylate species which were not grafted onto polyethylene. The difference in weight before polymerization and after extraction was regarded as the net amount of polymethacrylates grafted onto polyethylene.

High energy radiation gives rise in main chain scission and cleavage of ester groups in polymethacrylates [9]. By extraction with methanol small molecules and low-molecular products are removed [8]. In this way, one may get insight into the degree of side group splitting and of low molecular weight products. Extraction with xylene removes the decomposed products with higher molecular weight from the network. Figures 2 and 3 show the dependence of weight loss of PMMA, PEMA

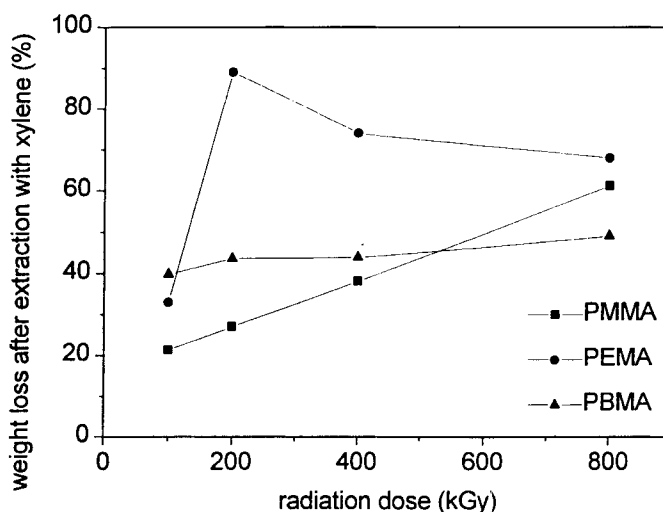


Figure 3. Dependence of total weight loss on the radiation dose.

and PBMA on irradiation dose after extraction with methanol and xylene, respectively

Both Figures 2 and 3 show an increase in weight loss with the irradiation dose. While the degradation to low molecular products for PEMA and PBMA increases almost linearly with radiation dose, the degradation of PMMA is rapid at first and then it slows down. Although the absolute amounts were low (less than 10%), PMMA degrades clearly more than its counterparts. The curves for the weight decrease after extraction with xylene appear complicated. While the weight decrease for PEMA shows a maximum at 200 kGy, the amount of weight decrease for PBMA seems just slightly dependent on irradiation dose. In contrast PMMA gives a linear relationship. The reason for this remains still unclear.

Influence of Irradiation on PDMA

Due to its long ester groups dodecyl methacrylate is a good solvent for PE, which is the prerequisite for the *in situ* synthesis of this work. It was believed that PDMA would crosslink instead of degrade under irradiation because of its long ester groups [10]. IPN films consisting of 1:1 ethylene and dodecyl methacrylate units were prepared. The samples were extracted with xylene to remove the soluble parts (12.7 wt%) and then subjected to irradiation at different doses. A notable decrease in weight was detected within the samples. Figure 4 shows that the amount

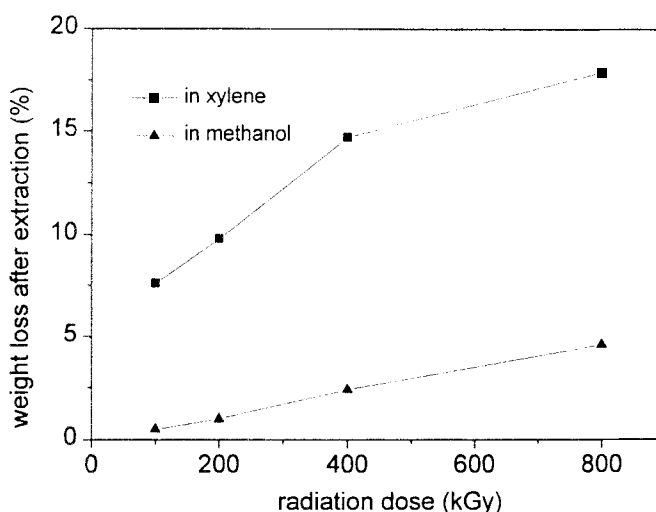


Figure 4. Dependence of degradation of PDMA on the radiation dose.

of degradation increases with irradiation dose. At 800 kGy the weight loss in xylene reached 17.9%. The weight loss by extraction with methanol gives a straight line with a value of 4.6% at 800 kGy

Influence of Electron Beam Irradiation on Gel Content

In Table 1, the results of extraction with methanol and xylene for the unirradiated samples are listed. No definite differences in the residual amount after methanol extraction is noticeable among different IPN systems. That is, the difference in conversion of polymerization reaction was small for the studied IPN systems. However, the gel contents for systems prepared with addition of BDDM were obviously higher than their counterparts prepared without BDDM. In these materials the incorporation of the dimethacrylate results in an almost complete crosslinked material. The differences become smaller when the IPN systems contain DMA which are crosslinked not only by the BDDM but also by peroxidic crosslinking of the long aliphatic ester side chains [5].

In fact, systems prepared without divinyl crosslinker are not real IPN since no methacrylate network can be formed. However, all studied materials have a high gel content which is caused by the crosslinking of the aliphatic side chains of the methacrylates and by the grafting of the methacrylates onto the peroxidic crosslinked PE phase. The extent of side chain crosslinking obviously depends on their length.

TABLE 1. Composition of the IPN Systems and their Insoluble Parts in Methanol (MeOH) and Xylene (Gel Content) Before and After Irradiation with 800 kGy

Sample	Composition	Molar ratio of	PE	BDDM	Insoluble	Gel	Insoluble	Gel
		methacrylate			in MeOH	content	in MeOH	content
		mol%	wt%	mol%	wt%	wt%	wt%	wt%
M-1	PE/BMA	100	16,47	-	90,9	55,6	74,0	37,3
M-2	PE/BMA	100	16,47	1	93,0	84,4	94,8	72,9
M-3	PE/(DMA/EMA)	20/80	16,45	-	94,0	79,8	79,0	27,6
M-4	PE/(DMA/EMA)	20/80	16,45	1	93,1	87,3	89,5	74,9
M-5	PE/(BMA/EMA)	50/50	17,93	-	90,9	45,5	47,8	38,6
M-6	PE/(BMA/EMA)	50/50	17,93	1	93,4	80,8	72,3	57,3
M-7	PE/(DMA/MMA)	20/80	17,61	-	93,8	77,9	58,7	43,1
M-8	PE/(DMA/MMA)	20/80	17,61	1	94,7	88,8	88,7	77,4
M-9	PE/(BMA/MMA)	50/50	18,77	-	92,7	51,7	28,6	24,5
M-10	PE/(BMA/MMA)	50/50	18,77	1	93,2	86,3	81,7	65,0

Samples for irradiation were extracted with methanol beforehand in order to exclude the effect of extractable contents in the sample. The insoluble parts in methanol and xylene after irradiation with 800 kGy are given in Table 1. Samples prepared with addition of BDDM have a significant higher content of insoluble decomposition products than the products prepared without BDDM addition. The high crosslinking degree diminishes the possibility of the formation of the extractable products.

Comparing the values in Table 1, it is seen that the greatest changes in gel content took place between unirradiated and irradiated samples which contained DMA without BDDM (M-3 and M-7). The gel content of unirradiated M-3 was 79.8%. It is reduced to 27.6% after the sample was irradiated. The gel content of irradiated M-7 was 34.8% lower than that of the unirradiated sample. Therefore, it is assumed that polymethacrylates used in this work (even those with long chained ester groups) degrade more than crosslink, which is in accordance with the results obtained from PE/PDMA, but contrary to reference [10].

The scissioning efficiencies for polymethacrylates increase in the order PBMA, PEMA, PMMA [7]. The same order is obtained from the extraction results for the series M-1 (PE/PBMA), M-5 (PE/BMA-co-EMA), and M-9 (PE/BMA-co-MMA) and the series M-3 (PE/DMA-co-EMA) and M-7 (PE/DMA-co-MMA).

Morphology of Irradiated Surface

The morphology of the IPN thin films M-6 is shown in dependence on the processing step in Figures 5 to 8. Figure 5 is the micrograph of the surface of the virgin IPN M-6. The surface is rather smooth. After extraction with xylene the surface appeared in a characteristic relief structure but still tight (Figure 6). Figure 7 is the micrograph of irradiated M-6 which was taken after the extraction with xylene. It is obvious that the surface of the sample is no longer tight and that some parts of the material were removed, leaving pores of about 200 nm, which is attributed to the degradation of the polymethacrylates. Figure 8 is the micrograph of irradiated M-6 on the cross section which was prepared by cryofracturing in liquid nitrogen. It shows also pores similar to those in Figure 7.

Flux Measurement

One of the prerequisites for the microfiltration or ultrafiltration is that the pores are interconnected. Flux measurements are selected as a method to characterize the membrane properties of the resulted materials. Ethanol was used to investigate the permeability because the samples are hydrophobic. Samples of series PE/BMA-co-MMA containing 50 mol% of MMA are very brittle and it is not possible to determine their membrane properties by flux measurements.

So far, most of the samples of series PE/DMA-co-EMA were permeable to ethanol, though some showed weak mechanical strength. The flux values varied from 0.42 to 109.8 l/m²h at 2 bar. IPN of PE/DMA-co-EMA were prepared with various contents of BDDM and Trigonox-101. However, a relationship between the synthesis conditions and flux could not be determined yet. The reason for this might be the complex process of phase separation during the network formation. Some minor changes during the synthesis can dramatically affect the final phase structure and thus the membrane morphology.

CONCLUSION

The crosslinking of low density polyethylene was carried out both by irradiation and by peroxide initiation. The irradiation of the polyethylene previously crosslinked by peroxide only raised the gel content from 91.3% to 93.2%.

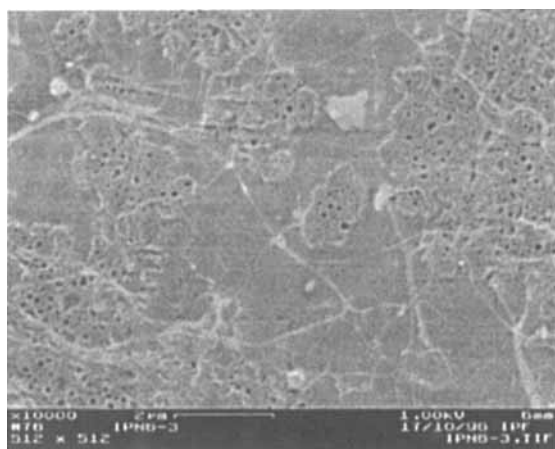


Figure 5. Micrograph of the surface of the IPN thin film M-6 after preparation.

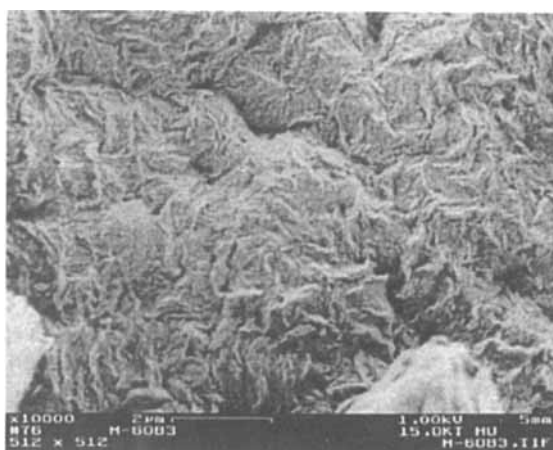


Figure 6. Micrograph of the surface of the IPN thin film M-6 after extraction with xylene.

A gravimetric method was introduced to investigate the degradation behavior of the individual polymethacrylates in the immediate presence of polyethylene. The incorporation of the divinyl methacrylate in the IPN restrains the destruction of the polymer networks under irradiation and thus raises the gel contents. Polymethacrylates used in this work (regardless of the length of ester group) degrade under irradiation more than crosslink. The amount of degradation of

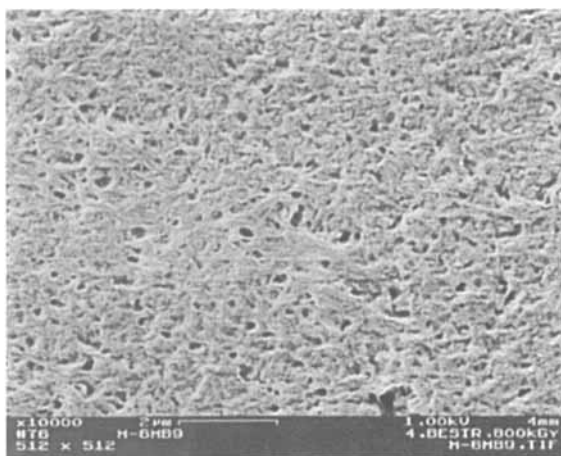


Figure 7. Micrograph of the surface of the IPN thin film M-6 after irradiation and extraction with xylene.

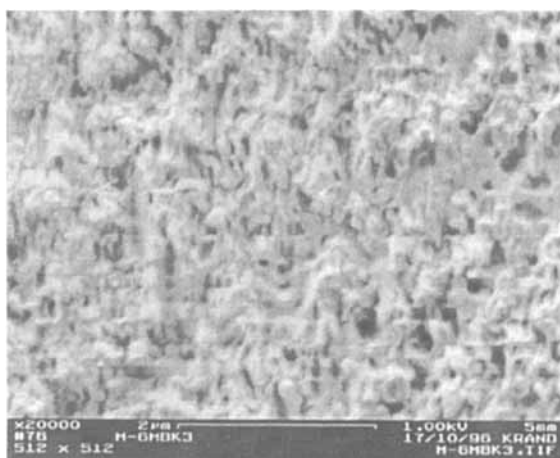


Figure 8. Micrograph of the cross section of the IPN thin film M-6 after irradiation and extraction with xylene.

polymethacrylates is dependent on the scissioning efficiency which is in the order PMMA>PEMA>PBMA.

Each type of polymethacrylates shows a characteristic degradation pattern. In contrary to literature it was found that PDMA degrades also under irradiation.

Morphology observation of the irradiated materials shows that pores of about 200 nm were formed by xylene extraction. Samples permeable to ethanol were obtained, implying the possibility to use them as membrane materials.

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