Gas-Phase Photoinduced Graft Polymerization of Acrylic Acid onto Polyacrylonitrile Ultrafiltration Membranes*

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SYNOPSIS

Heterogeneous surface modification of polyacrylonitrile (PAN) ultrafiltration (UF) membranes is realized with UV irradiation-initiated graft polymerization of acrylic acid (AA) from the gas phase onto photoinitiator (benzophenone, BP)-coated samples. In the absence of monomer, PAN functionalization by ketyl radicals dominates after UV excitation of sorbed BP. With AA, graft and total polymer yield increase with BP loading and UV irradiation time. Average molecular weight and distribution of PAA homopolymer—formed in parallel during graft polymerization—are analyzed with gel permeation chromatography. Morphology of PAN-gr-AA UF membranes is checked with scanning electron micrographs (SEMs) and atomic force microscopy. Chemical changes are characterized with FTIR-ATR spectroscopy and SEM/EDX analyses, indicating a pronounced surface selectivity of the graft polymer modification (localized in the upper 5-μm membrane thickness). The amount of grafted PAA systematically reduces membrane permeability and increases dextrane retention, as verified in UF experiments. Photo graft polymer modification of UF membranes will be applied to adjust membrane performance by controlling surface hydrophilicity and permeability using other monomers and/or further graft polymer functionalization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Modification of synthetic polymer membranes by postformation treatment is a common and convenient way to make them better suited for special applications. In ultrafiltration (UF), adjustment of membrane surface hydrophilicity/hydrophobicity balance is of great importance, e.g., for protein separations[1] and to reduce membrane fouling.[2] Alternative techniques for producing composite membrane structures based on suited UF membranes are still very attractive. Such novel membranes can be applied, e.g., in affinity UF,[1,3] nanofiltration,[4] or pervaporation.[5]

Important advantages of photoreactions are their chemoselectivity under mild conditions, and the option to induce reactions in thin layers of large area. Methods such as controlled photodegradation[6] or heterogeneous photofunctionalization[7–10] become increasingly interesting for defined modifications of polymer surfaces. Because of high quantum yields and reaction rates, photopolymerizations are especially efficient. Using various photosensitizers, graft polymerizations of monomers from the gas phase or from solutions onto some synthetic polymers—films or fibres—have been realized.[11–16] Also, intrinsic photoreactivity of polymers[17] and/or photoinduced peroxide formation[18] can be used to initiate surface graft polymerization. Photo graft polymerization variants have perspective for application in continuous production processes.[19]

Nevertheless, only a limited number of papers deal with photochemical modifications of synthetic separation membranes. Principally, photosensitive polymers can be used as membrane material. How-

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ever, this approach is difficult because of changed membrane-forming properties as compared with the parent membrane polymers.[20,21] Modification of membrane properties as result of photoreactions has been studied, e.g., with composite reverse osmosis membranes containing α-diazo-carbonyl groups,[20] pervaporation membranes from 2H-tetrazolyl modified ABS,[22] and UF membranes made from brominated polyacrylonitrile (PAN).[21] On the other hand, already optimized, commercial membranes can be used as substrates. Membrane polymer photodegradation was postulated as an initiating step during polymer grafting hydrophilization of polysulfone UF membranes induced by UV irradiation.[23] Chemical surface functionalization of PAN UF membranes has been realized using photolysis of various substituted aryl azides.[9] Possibilities of photopolymerizations for membrane modification have been explored intensively by Zeni et al.[24] and Selli and Bellobono.[25] Basically, these authors used benzoinether-sensitized photo graft polymerization and crosslinking of epoxy diacrylates onto, e.g., cellulose microfilters to immobilize, e.g., zeolithes[24] or enzymes.[25] The resulting membranes were used as ultrafilters with additional sorption[24] or biocatalytic properties.[25] The same concept had been applied to produce pervaporation membranes based on polysulfone membranes.[5]

We used ultrafiltration membranes—made by phase inversion from polyacrylonitrile[26]—as substrates. PAN is an attractive material because of its moderate hydrophilicity and comparatively high thermal and chemical stability. There are "conventional" chemical methods to modify PAN (for a review, cf. Silbermann[27]), but it is difficult to apply them for membranes without changing the preformed porous structure.[28] Grafting onto solid PAN homopolymer is not common.[29] Just recently, a first report on photoinduced graft polymerization of methacrylates onto PAN fibres appeared in the literature.[30]

The aim of our studies is to demonstrate that by heterogeneous photochemically induced reactions it is possible to change chemical structure and separation properties of the active layer of UF membranes, under mild conditions and consequently without damage of the sublayer pore structure (cf. Ulbricht and Hicke[31]). Here we report on a heterogeneous modification procedure for PAN UF membranes by UV irradiation-initiated graft polymerization of acrylic acid (AA) from the gas phase onto photoinitiator-coated samples (for a preliminary note, cf. Oechel et al.[32]). The membranes were coated with benzophenone from methanolic solutions, then UV irradiated in an atmosphere of AA, and finally extracted to remove homopolymer. The influence of initiator loading, and of irradiation time and wavelength on graft and total polymer yield were determined. Homopolymer was analyzed with HP gel permeation chromatography (HP-GPC). The morphology of PAN-gr-AA UF membranes was checked with scanning electron micrographs (SEMs) and atomic force microscopy (AFM). Chemical changes were characterized with FTIR-ATR spectroscopy and SEM/EDX analyses. The influence of graft polymer on permeability was studied in UF experiments.

EXPERIMENTAL

Materials

Membranes were prepared by a continuous solution casting/immersion precipitation process with polyacrylonitrile (PAN; M_W = 135,000 g/mol, M_n = 35,000 g/mol; BUNA AG, Germany) solution (17.5 wt %) in dimethylformamid as 0.2 mm film on a polyester backing, and water as precipitation medium.[26] Dried membranes without the backing material were used for all experiments. Acrylic acid (99+%), benzpinacol (99%), diphenyl carbinol (99%), copper hydroxide (p.a.), and sodium hydroxide (p.a.) were purchased from Aldrich (Steinheim, Germany) and used as received. Benzophenone (Laborchemie Apolda, Germany) was recrystallized twice from ethanol. Nitrogen (TEGA Technische Gase GmbH, Berlin, Germany) was of high purity (99.9%). Methanol (HPLC grade) was purchased from Ferak (Berlin, Germany). Dextrane M 70 (M_w ca. 70,000 g/mol; Serumwerk Bernburg, Germany) was applied for membrane selectivity characterization. Water purified with a Milli Q system (Millipore GmbH, Eschborn, Germany) was used for all experiments.

Analytical Equipment and Methods

For all gravimetric determinations a microbalance (MP 20; Feinmechanik, Freiberg, Germany) was used. UV-Vis spectra were recorded with a model PU 8735 (Pye Unicam, Cambridge, UK). FTIR-ATR spectra were obtained using a model 1760 (Perkin-Elmer Corp.) equipped with an ATR unit (KRS 5 crystal; 45 degrees, 14 reflections; L.O.T. GmbH, Darmstadt, Germany) using the MCT detector and 125 scans at a nominal resolution of 4 cm^{-1}. The HPLC system was set up with either two pumps LC-6A or one pump LC-9A, autoinjector SIL-6B,

column oven CTO-6A, UV detector SPD-6AV or RI detector RID-6A, and integrator CR-4-AX (all Shimadzu, Kyoto, Japan). Samples for SEM were prepared by breaking specimens carefully in liquid nitrogen and sputtering with gold, and were then analyzed using a model JSM 840A (Jeol Corp.) equipped with a Kevex Delta Energy Dispersive X-Ray Spectrometer (detection of elements > B with ca. 0.5% accuracy), usually at 15 keV and 0.5 nA. A Nanoscope III AFM (Digital Instruments, Santa Barbara, CA, USA) with microfabricated silicon nitride cantilever was used in the constant deflection mode. Imaging was done in air with a 2-μm scanner.

Photo Modification Procedure

Membrane Coating with Benzophenone

Preweighed membrane samples were immersed in benzophenone (BP) solutions in methanol (10–100 mmol/L) and shaken for 18 h at about 23°C. The samples were taken out and, after adhering solution was removed by touching slightly with filter paper, dried at about 23°C in a desiccator over P_4O_{10} and BP. In order to determine the concentration dependence of initiator uptake, BP-coated samples were weighed or/and extracted with methanol. BP con-

centrations were determined UV-spectroscopically (ε [BP, MeOH; 235 nm] = 7225 L/mol cm).

Photo Graft Polymerization of Acrylic Acid

The experimental set-up is summarized in Figure 1. Membrane samples were placed in the center of a thermostatable reaction chamber (diameter: 100 mm) with gas entrance and exits, equipped with either a glass or a quartz window (thickness: 4 mm; also serving as a light filter, λ_{exc} > 320 nm or λ_{exc} > 220 nm) for UV irradiation (customer-designed reactor built by Normag Laborglas & Verfahrenstechnik GmbH & Co., Hofheim, Germany). A laboratory-scale Deep UV Illumination System (220–260 and 260–320 nm; 87000 STD-1; L.O.T.-ORIEL Corp., Darmstadt, Germany), equipped with a high-pressure mercury lamp (HBO 350 Deep UV, Osram, Berlin-München, Germany) and providing homogeneous illumination (±5%) of up to 180 cm^2 surface area, was used. Distance between the collimating lens of the UV system and the sample was 150 mm, giving an irradiation dose of about 3.0 mW/cm^2 (with glass window; measured with Optical Power Meter Model 371, equipped with Detector Head 268UVA; United Detector Technology, Hawthorne, CA, USA). Graft polymerization was realized as fol-
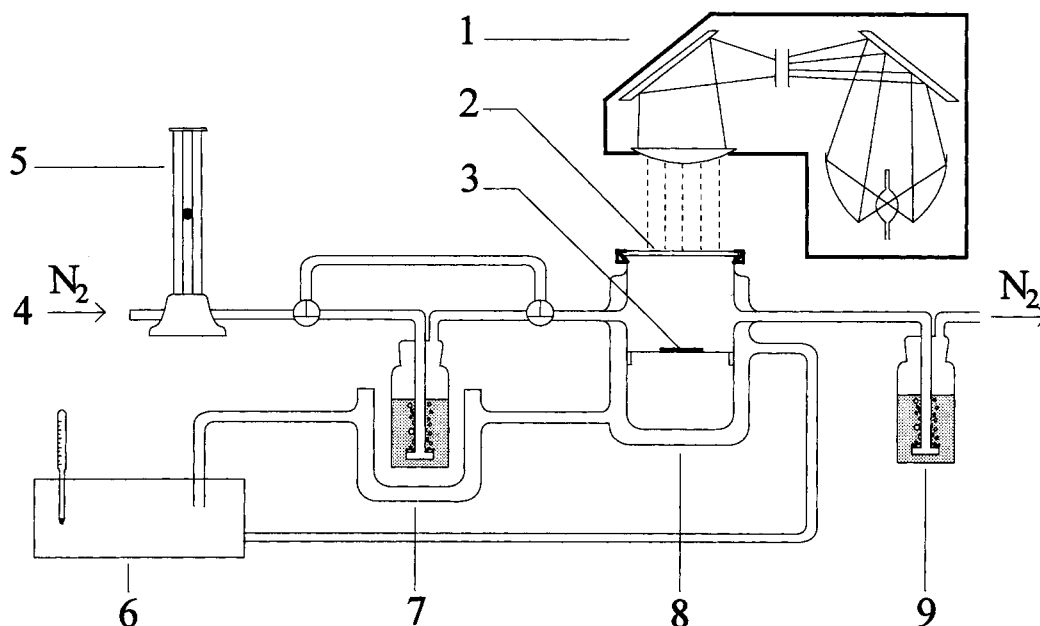

Figure 1 Experimental setup for gas phase photo graft polymerization onto membranes: 1) Illumination system, including UV lamp HBO 350, quartz mirrors, and collimating lens; 2) reactor light entrance window (glass or quartz, exchangeable); 3) membrane sample; 4) gas supply from nitrogen tank; 5) flow meter; 6) thermostat; 7) temperature-controlled monomer reservoir; 8) temperature-controlled reactor; 9) exiting monomer sorption bottle.

lows (cf. Fig. 1): The reaction chamber (kept at 65°C) was purged with nitrogen (10 L/h) for 15 minutes. Then, an acrylic acid (AA) vapor atmosphere was created by bubbling nitrogen (10 L/h) through the reservoir containing pure monomer (maintained at 65°C). UV irradiation for various amounts of time was started after 15 minutes. AA leaving the reaction chamber was sorbed in a gas washing bottle, filled with 0.1N NaOH solution. Monomer gas phase concentrations of 13–19 mg/L were calculated from the results of AA titration and gas flow rate. After irradiation, the reactor was purged with nitrogen again for 15 minutes, then samples were taken out, dried over P_4O_{10} and weighed to determine the total polymer yield. The membranes were extracted twice with water for 8 hours using a Soxhlet apparatus, then dried and weighed again to determine the graft polymer yield. Total (TY) and graft polymer yields (GY) were calculated according to:

$$TY = (m_t - m_o)/m_o * 100\%;$$

$$GY = (m_{gr} - m_o)/m_o * 100\%$$

with m_o as the initial membrane sample weight, m_t as the weight after grafting, and m_{gr} the weight after grafting and extraction. Using the same modification conditions, the reproducibility of TY and GY was better than ±10%. GPC analyses of homopolymer extracts were performed with a Nucleogel-aqua OH 40 column (Macherey-Nagel, Düren, Germany) and 0.1M NaNO$_3$ solution in water at 32°C and 1.0 mL/min flow rate using the RI detector. PEG and PEO standards (from calibration kits PEG-10 and PEO-10, respectively; Polymer Laboratories Ltd., Shropshire, UK) were used for calibration, and the set of retentions obtained (e.g., PEG 4100: 9.71 min; PEG 23,000: 8.58 min; PEO 150,000: 7.36 min) was used for approximate M_w determination of PAA (cf. Bahary and Jilani[33]).

Photoreactions of Membrane-Sorbed Benzophenone

For analytical studies, preweighed BP-coated PAN membranes were irradiated in a nitrogen atmosphere (10 L/h gas flow rate), then extracted with methanol, and thereafter dried and weighed again. The extracts were analyzed with HPLC. Separation was realized with a column ET 250/8/4 Nucleosil 5 C_{18} (Macherey-Nagel, Düren, Germany), methanol/water (70/30, v/v) at a flow rate of 1.0 mL/min at 40°C; the UV detector was set at 235 nm.

Ultrafiltration Experiments

For UF characterization experiments, stirred cells were used with 50 or 10 mL volume and 13.4 or 4.1 cm^2 active membrane areas, respectively (Models 8050 or 8010, respectively; Amicon GmbH, Witten, Germany). Membrane samples were pressurized with water at 0.3 MPa for 30 minutes, then pressure was reduced to 0.2 MPa and water flux measured by timed collection until a stable value J_w was observed. In selected cases the pressure was varied between 0.05 and 0.4 MPa by stepwise increasing and decreasing (twice), in order to check pressure dependence of permeability. Filtrate flux J_f for dextrane solutions (c_o = 1 g/L in water) was measured at 0.2 MPa by timed collection of filtrate samples, which were then analyzed for sugar concentration with a polarimeter (model 241, Perkin-Elmer Corp.); dextrane retention R was calculated according to:

$$R = (c_{ret} - c_{filtr})/c_{ret} \times 100\%$$

with c_{filtr} dextrane concentration in the filtrate fractions, and c_{ret} dextrane concentration in the retentate (calculated from c_o, and c_{filtr} using the mass balance).

RESULTS AND DISCUSSION

Membrane Coating with Photoinitiator

In order to enable graft polymerization of acrylates on PAN membranes, chemical surface activation is necessary. Benzophenone (BP) was selected as photoinitiator, because after UV irradiation it can efficiently create polymer radicals via H abstraction,[34] hence it is frequently used in such applications.[11,13–15,17,30] Different variants to apply the initiator had been realized previously in heterogeneous surface grafting: (a) dispersion of initiator in the polymer before film preparation,[11] (b) sorption onto the surface from the gas phase or from solutions (soaking) and subsequent solvent evaporation,[11,12,15,16,19,30] (c) coating the surface with the initiator suspended in another polymer which is considered as inert toward grafting,[13,14] and (d) application together with monomer from the gas phase or from solution.[15,16,19] In our studies a simple coating procedure (item (b), above) was applied because: (1) BP as an additive in the membrane casting solution (cf. (a)) changes properties of the prepared membrane; (2) an additional polymer layer (as in (c)) could irreversibly damage the microporous membrane structure;

(3) homopolymerization (expected with (d)) should be limited as much as possible.

Membranes were soaked in solutions of BP in methanol, a solvent which does not change the membrane pore structure and can easily evaporate. The initiator loading depending on BP solution concentration is shown in Figure 2. A steady increase of initiator loading with BP solution concentration was observed. The specific pore volume of the membranes was determined from the weight differences of water-wet and dry PAN membranes as 2.88 cm³/g. Using that value, the amount of BP which had been simply captured with solution in the pore volume can be calculated (288 μmol/g for 100 mM BP solution). The solution concentration dependence of this amount is also plotted as a line in Figure 2. It can be seen that the BP uptake is slightly higher than due to inclusion within the pore structure only; this can be attributed to adsorbed BP. An attempt— in analogy to Ulbricht and Hicke[9]—to determine the adsorbed BP amount directly from isotherms was not successful. Hence it may only be estimated that for low BP loading (obtained from 10 mM BP solutions), about 40% of the initiator is adsorbed on the membrane surface. The adsorbed amount seems to become smaller with increased total loading (for 100 mM BP in solution; Fig. 2), which is not reasonable. Perhaps, not the entire pore volume is accessible for BP from higher concentrated solutions. Note that in other applications of BP for surface photo grafting, the exact initiator loading and distribution have not been determined.[12,15,16,19] For coating times of 2 h and longer, no significant influence of time on BP uptake was observed. Hence, for
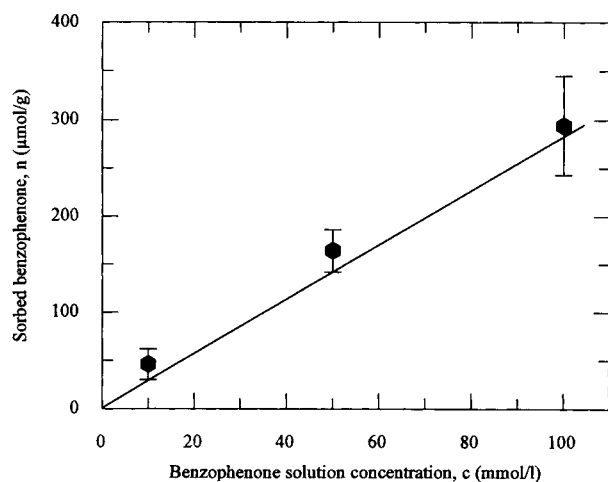

Figure 2 Amounts of benzophenone (BP) on PAN UF membranes (photoinitiator loading) obtained after coating from methanolic solutions of varied BP concentrations (16 h) and drying.

graft experiments, a loading time of at least 2 h was applied and the BP amount was checked for each membrane sample immediately before grafting.

UV-Induced Conversion of Initiator Sorbed on PAN UF Membranes

Besides application of benzophenone in polymer grafting and degradation studies dealing with effects on polymers, there is only limited knowledge about BP conversion, in particular the soluble and insoluble products formed after UV irradiation of BP dispersed in or sorbed on solid polymers. The major path of BP photoreaction in H donor solutions is the formation of ketyl radical-derived products with pinacol structure, e.g., for high stationary ketyl concentrations, the dimer benzpinacol BDP[34] (cf. Scheme 1). Formation of more complicated and less stable structures, so-called "light absorbing transients" (LATs), derived from chinoid radical isomers has also been verified.[35] Already, in the earliest work on photografting (onto solid polyethylene) Oster et al.[11] concluded that polymer functionalization may take place; the only soluble BP product seemed to be benzoic acid BA. In a series of IR studies on BP photolysis in various elastomers, basically three product groups—with yields depending on polymer structure and morphology—were detected: (a) benzpinacol BPD, (b) other soluble ketyl radical products (derived from LATs), and (c) various polymer functionalization products described as grafted LATs[36] (cf. Scheme 1).

BP-coated PAN membranes were UV irradiated in a nitrogen atmosphere and extracted, and the extracts analyzed with HPLC. Chromatographic conditions were selected to achieve clear separation of BP from hypothetic soluble photolysis products such as benzpinacol (BPD), diphenyl carbinol (BC), and benzoic acid (BA) (cf. Scheme 1). 228 μmol/g BP were found before, and 82 μmol/g after, UV irradiation (60 min) of samples with identic BP loading. Other products were found in very small amounts and could not be identified (e.g., a substance with an HPLC retention very close to BC; using the calibration for the diphenyl methane chromophore of DC allowed a concentration estimate of 2 μmol/g). Not even traces of BPD, BC, or BA could be detected.

FTIR-ATR spectra of PAN membranes, after coating with BP (1300 μmol/g), subsequent UV irradiation, and extraction, are presented in Figure 3. Qualitatively similar data were also obtained for lower BP loading and varied irradiation time. The initiator BP can be identified with help of its char-
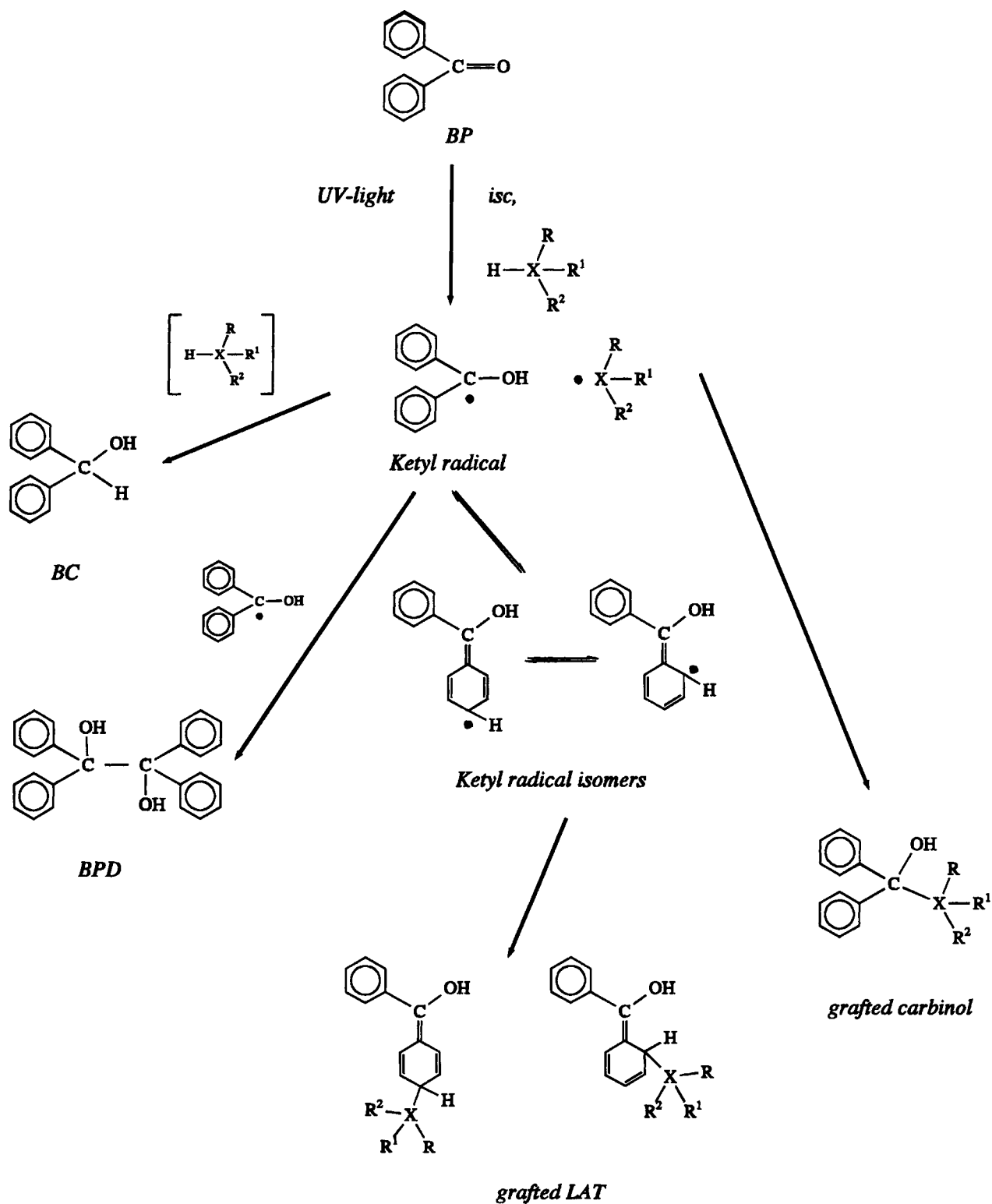
R, R^1, R^2: Polymer backbone and functional groups

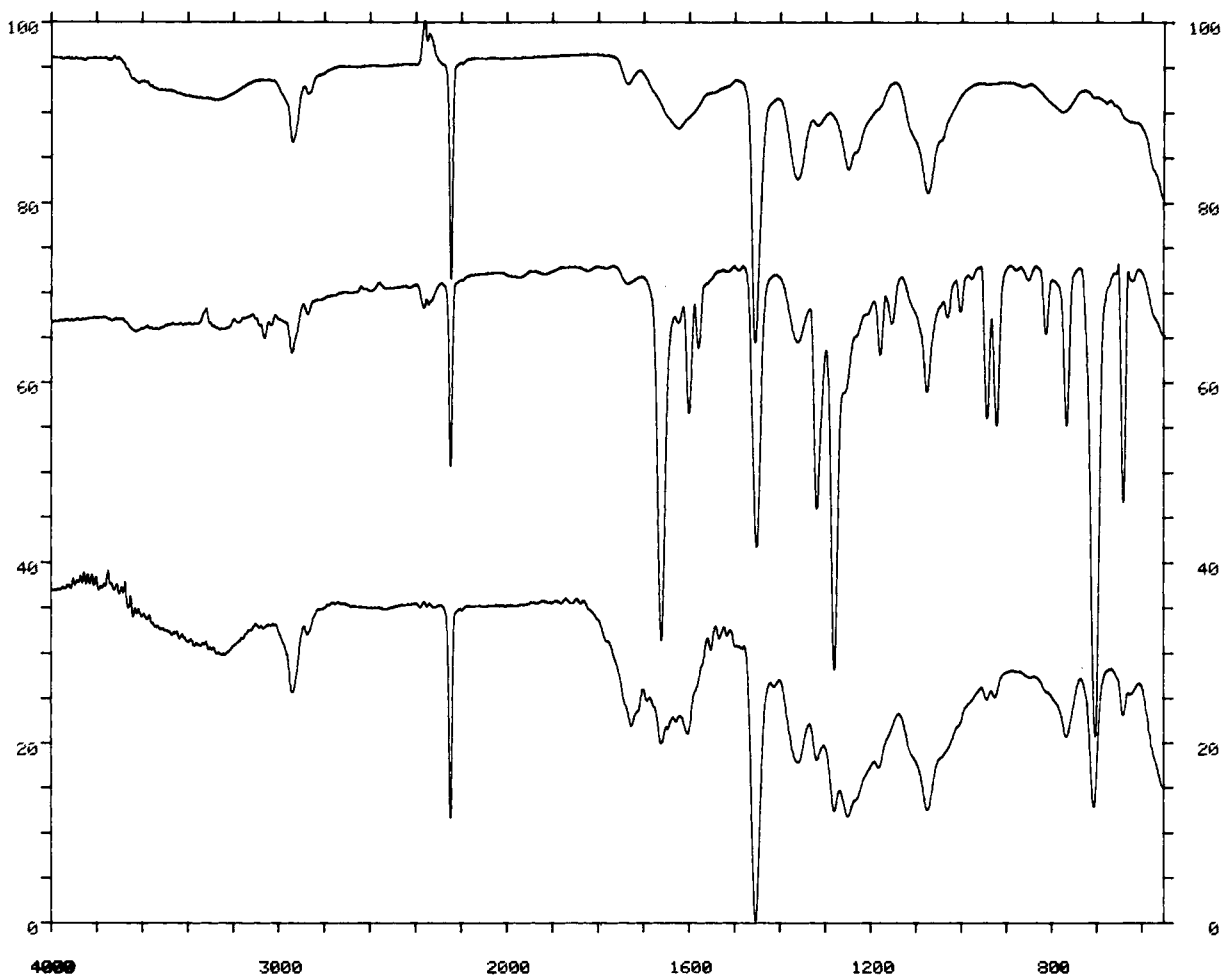**Scheme 1**   Reaction pathways after photoexcitation of benzophenone.

Figure 3   FTIR–ATR spectra of active surface of PAN UF membranes (KRS 5, 45 degree):
(a) parent sample; (b) after coating with BP (1300 μmol/g); (c) same as (b), and after 60
min UV irradiation ($\lambda_{exc} > 320$ nm) and extraction—"BP functionalization."

acteristic carbonyl ($\nu_{C=O}$ at 1660 cm^{-1}), and aromat ($\nu_{C=C}$ at 1600 cm^{-1}, δ_{CH} between 950 and 700 cm^{-1}) absorptions. Interestingly, after UV irradiation and extraction, the aromatic bands are still present in reduced intensity, while new broad bands in the carbonylic region (around 1720 cm^{-1} and 1660 cm^{-1}) and—with little intensity—around 3200 cm^{-1} are observed. With our ATR data (cf. Fig. 3), a qualitative interpretation in terms of functionalization product structure (diphenyl carbinol derivative vs. LAT product, cf. Scheme 1) will not be attempted. However, it is obvious that besides surface functionalization, PAN conversion also takes place, giving rise to the additional new bands in the carbonylic region. Under the same conditions, short-wavelength UV irradiation ($\lambda_{exc} > 220$ nm; up to 120 min) of PAN UF membranes caused very similar changes in IR-ATR spectra, while after long wavelength excitation ($\lambda_{exc} > 320$ nm) no change could be observed.

This leads to the conclusion that selective excitation of BP—similar to direct PAN excitation—induces polymer degradation, presumably the PAN specific "cyclization" and oxidation reactions (cf. Friedländer et al.[37] and Skowronski et al.[38]).

The results can be discussed as follows. Because only 36% of the BP amount originally coated on the membranes could be detected in extracts, and other unidentified soluble products were present only in very small amounts, functionalization of the membranes must have taken place. Indeed, in IR-ATR spectra a functionalization could be observed; namely, aromatic groups were introduced into the surface structure of the membrane polymer. On the other hand, the characteristic dimerization product after BP photoreaction, BPD, could not be observed. Consequently, the typical reaction of BP after UV excitation—H abstraction from the polymer matrix yielding polymer and ketyl radicals—may take place.

However, due to the low mobility of BP in the adsorbed and sorbed states, recombination of the radical pair seems to be the dominating further process. Other bimolecular reactions of ketyl radicals, such as dimerization (BPD formation) or a second H abstraction (BC formation), are not favored (cf. Scheme 1). However, PAN degradation ("intramolecular" cyclization) and oxidation are possible.

Photo Graft Polymerization of Acrylic Acid onto Initiator-Coated PAN Membranes

Benzophenone-coated PAN UF membranes were grafted with acrylic acid (AA) from the gas phase, using the experimental setup illustrated in Figure 1. AA gas phase concentrations of 16 ± 3 mg/L were realized and not considered as variable. The influence of oxygen was reduced by creating a nitrogen atmosphere. BP loading of PAN membranes, and UV irradiation wavelength ($\lambda_{exc} > 220$ nm or $\lambda_{exc} > 320$ nm) and time were varied. All polymerization results are summarized in Table I. Without BP coating, only very little polymer formation on membrane samples could be detected after UV irradiation (up to 120 min) through the glass filter (long-wavelength UV excitation); using the quartz window (short-wavelength UV excitation), considerable polymerization was observed (cf. Table I). Selected data for selective excitation ($\lambda_{exc} > 320$ nm) are shown in Figures 4 and 5. Either increasing BP initiator loading with the same irradiation time (Fig.

4) or irradiation time with the same BP loading (Fig. 5) resulted in higher total (TY) and graft polymer yields (GY; cf. Table I).

Extractables were always formed, and could be identified as acrylic acid homopolymer (homo-PAA) with IR spectroscopy, acid titration, and gel permeation chromatography (HP-GPC, cf. Fig. 6). In all cases, higher amounts of homopolymer than of graft polymer were found (cf. Table I). Figure 6 shows GP chromatograms of extracts after AA grafting onto PAN membranes with varied BP loading under otherwise identical conditions. According to a calibration using PEG and PEO standards under the same chromatographic conditions (cf. Bahary and Jilani[33] and Experimental section), molecular weights between about 5000 and 150,000 g/mol are observed. For selective UV irradiation ($\lambda_{exc} > 320$ nm) with enhanced initiator loading on the membranes, increasing average M_w and broader distribution of homo-PAA were obtained (Fig. 6.1). Short-wavelength UV irradiation produced an even broader, bimodal M_w distribution indicating polymer chain scission (Fig. 6.2). Formation of shorter PAA chains under non-selective irradiation conditions ($\lambda_{exc} > 220$ nm), as compared with long-wavelength UV excitation, is also confirmed by comparison of chromatograms obtained for homo-PAA on membrane samples without BP (Fig. 6.3).

Figure 7 shows FTIR-ATR spectra of a parent PAN UF membrane, and of membranes after BP-initiated grafting before and after homo-PAA ex-

Table I Total and Graft Polymer (PAA) Yields and Estimated Surface Coverage S^1 with *gr*-PAA on PAN UF Membranes Dependent on Photoinitiator (BP) Loading, UV Irradiation Wavelength and Time

BP (μmol/g)	30 min UV:			60 min UV:			120 min UV:		
	TY (%)	GY (%)	S (μmol/cm²)	TY (%)	GY (%)	S (μmol/cm²)	TY (%)	GY (%)	S (μmol/cm²)
			$\lambda_{exc} > 220$ nm						
0				2.0	0.0	0	2.1	0.0	0
46	3.7	0.6	0.28	5.0	2.3	1.08	19.5	6.5	3.06
164	6.5	1.5	0.70	7.3	3.4	1.60			
294	8.2	1.8	0.85	11.0	4.2	1.97	18.4	7.2	3.38
			$\lambda_{exc} > 320$ nm						
0							0.1	0.0	0
46	2.3	0.3	0.14	2.8	0.5	0.24	3.5	0.6	0.28
164				7.3	0.6	0.28			
294	5.7	0.6	0.28	10.0	1.1	0.52	13.8	1.3	0.61

^{1} Surface coverage S was calculated from experimental GYs with the surface normalized weight of the PAN membranes of 3.34 mg/cm² thus assuming graft polymer modification of the outer membrane surface exclusively.
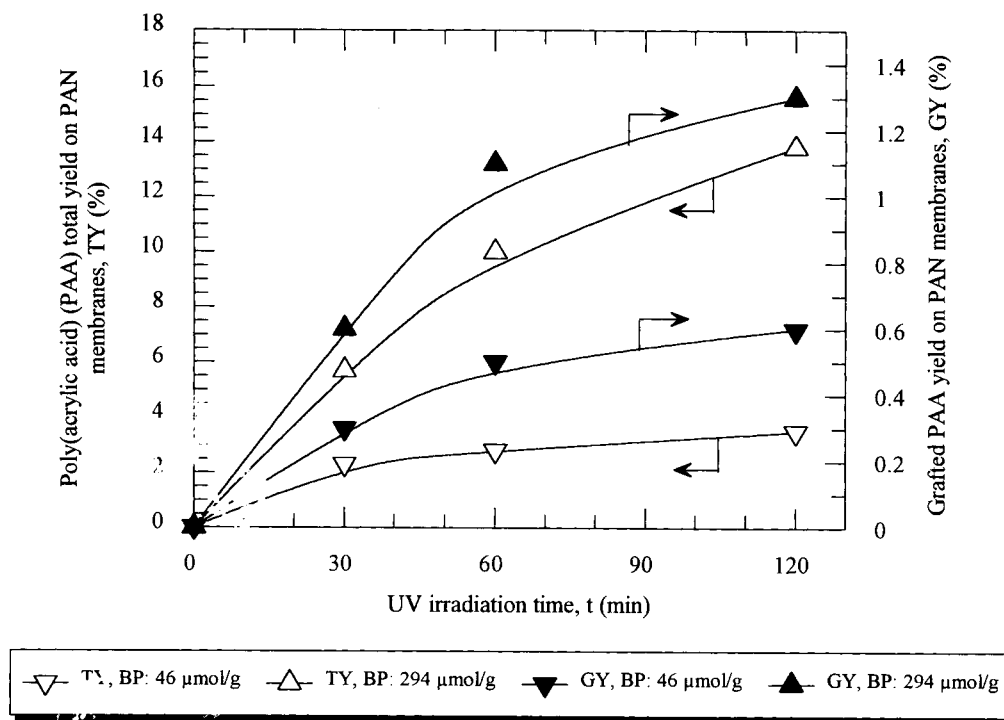
F:gure 4 Total and graft polymer (PAA) yields on PAN UF membranes dependent on UV irradiation time for two different photoinitiator loadings ($\lambda_{exc} > 320$ nm).

traction. The intense absorption of carboxylic groups ($\nu_{C=O}$ at 1710 cm^{-1}) dominates in the spectrum of samples directly after grafting. It is obvious from the low relative intensity of the nitrile band ($\nu_{C=N}$ at 2240 cm^{-1}) that PAA largely covers the sampled

surface region (Fig. 7[b]). Graft polymer (PAN-*gr*-AA) could also be clearly identified with ATR spectra (Fig. 7[c]). In addition, a correlation between graft yield (*GY*) and IR intensity of characteristic *gr*-PAA absorptions was observed (not shown).
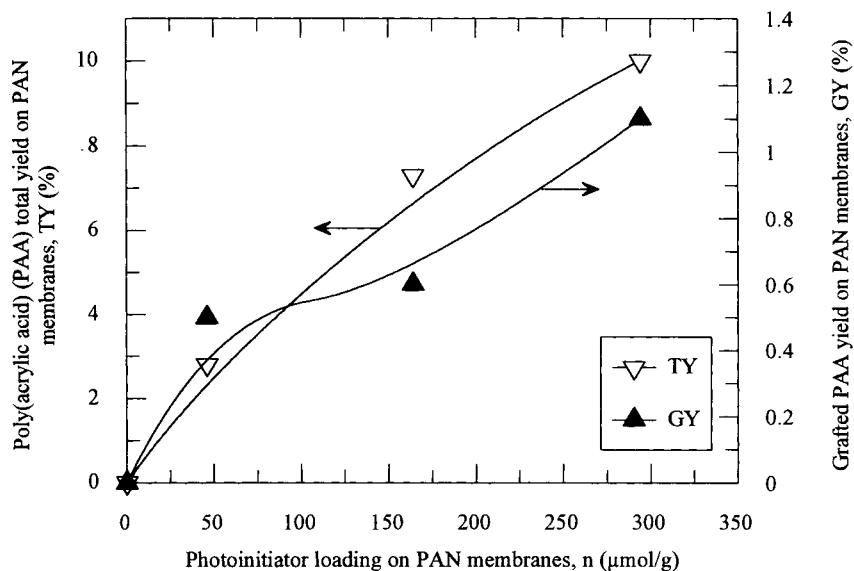

Figure 5 Total and graft polymer (PAA) yields on PAN UF membranes dependent on photoinitiator (BP) loading ($\lambda_{exc} > 320$ nm; 60 min.).
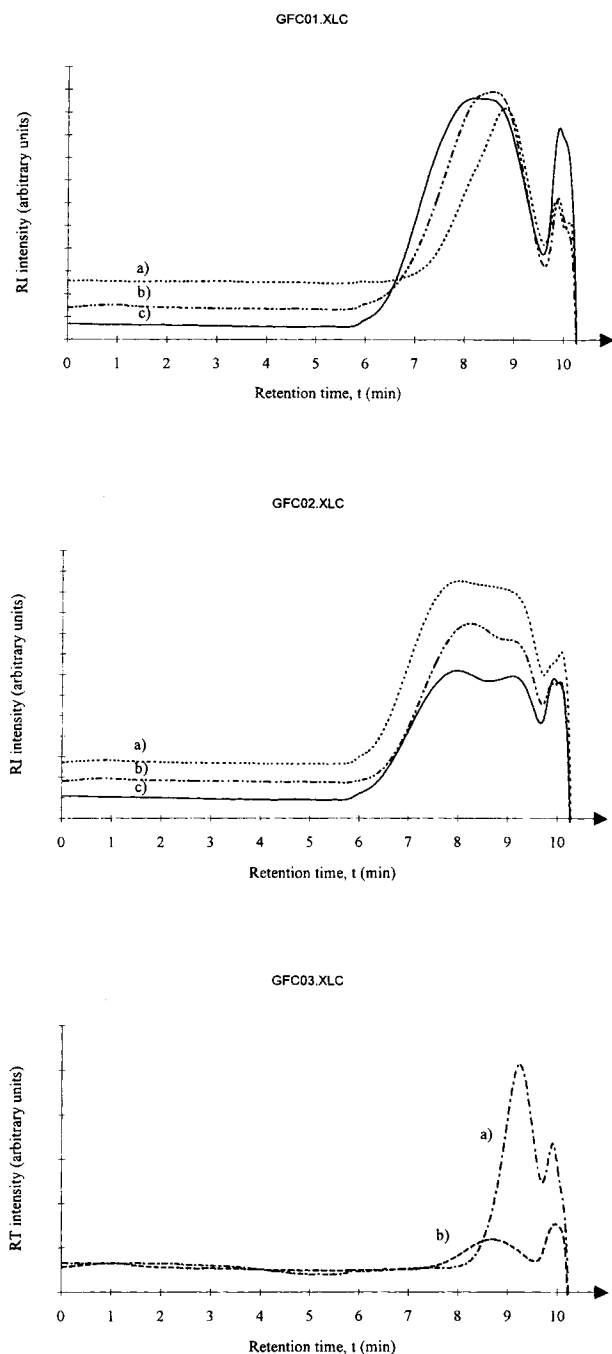
GFC01.XLC

GFC02.XLC

GFC03.XLC

Figure 6 High performance gel permeation chromatograms (HP-GPC) of extracts from PAN UF membranes—with varied photoinitiator loading—after photo graft polymerization modification with acrylic acid (AA); 6.1.: (a) 46 μmol/g, (b) 164 μmol/g, and (c) 294 μmol/g BP loading, respectively; λ_{exc} > 320 nm (solution concentrations 0.4, 0.7, and 1.0 g/L, respectively); 6.2.: (a) 46 μmol/g, (b) 164 μmol/g, and (c) 294 μmol/g BP loading, respectively; λ_{exc} > 220 nm (solution concentrations 0.8, 0.7, and 0.8 g/L, respectively); 6.3.: (a) λ_{exc} > 220 nm, and (b) λ_{exc} > 320 nm, respectively; no BP (solution concentrations 0.2, and 0.05 g/L, respectively).

In the IR spectrum of PAN-gr-AA (Fig. 7[c]), also the formation of BP functionalization products is clearly visible (δ_{CH} between 950 and 700 cm^{-1}; cf. Fig. 3). A correlation between the initial amount of BP loading and the intensity of those aromatic group absorptions was observed (not shown). These observations were confirmed by HPLC analyses of extracts after BP-initiated grafting of AA (for 60 min; also analyzed with GPC; cf. Fig. 6.1): 294 μmol/g BP were found before, and 190 μmol/g after, UV-induced AA grafting. Even if UV excitation conditions may be slightly different: the recovery of 65% BP in this experiment as compared with 36% from samples irradiated in the absence of AA (cf. above) indicates successful competition of monomer with ketyl functionalization of the membrane. Again, no other low molecular weight BP product, including BPD, could be identified.

An analysis of outer membrane surfaces was attempted with atomic force microscopy (AFM). BP-coated samples—partially behind a mask to prevent illumination of a particular region—were UV-grafted with AA under otherwise typical conditions, and then analyzed before and after homo-PAA extraction; the parent membrane is shown for comparison (Fig. 8[a]). The parent sample has the typical surface structure of this PAN membrane type.[26] PAN-gr-AA membranes after homopolymer extraction show a higher surface irregularity with domains of relatively low surface roughness (Fig. 8[b]) as compared with parent samples (Fig. 8[a]). In Fig. 8(c), a straightedge between two areas, one with similar morphology to parent PAN (cf. Fig. 8[a]) and one with significantly higher surface roughness can be identified. These two areas with different surface morphology, taken on the same sample directly after grafting, can be interpreted as the covered and the UV-exposed parts during the UV photomodification step.

Using FTIR-ATR with sampling depths of about 1 μm under applied conditions, no graft polymer modification could be detected on the support side of the membranes, indicating that this photomodification is indeed surface-selective. In SEM micrographs of cross sections and surfaces of PAN-gr-AA membranes—with GY up to 3%—no change of pore structure or indication of an extra layer on the outer surface was detectable. More-specific information about penetration depth of modification was expected from EDX spectra in cross sections of membranes sampled with SEM. Figure 9 shows EDX mapping analysis results of a PAN-gr-AA UF membrane with carboxylic acid groups converted into the copper salt in order to increase image contrast.

While parent PAN membranes contained only traces of oxygen with no indication of a concentration gradient and no copper, modified membranes were completely different: oxygen and copper were easily detected. Very high O and Cu intensities in a thin layer on and close to the active membrane surface were seen, while for nitrogen no significant intensity gradient with thickness was observed (cf. Fig. 9). The diminished N intensity in the top-layer region is an indication for reduced PAN concentration. A maximum depth of penetration for gr-PAA modification—introducing carboxylic groups able to bind Cu into PAN—of about 5 μm can be estimated from these data.

A discussion of several important aspects of the developed modification strategy follows. First, the graft polymerization of AA onto PAN is a *photoinitiated* process. Both photoinitiator *and* UV irradiation are essential, because in an AA atmosphere neither long wavelength irradiation of PAN membranes without BP (cf. Table I) nor covering BP coated samples during UV irradiation with a mask (cf. Fig. 8c) produces graft polymer. Using high energy, short-wavelength UV excitation yields less-defined modifications: direct homopolymerization is possible, and polymer photodegradation[38] can occur and may additionally cause either direct grafting or crosslinking (cf. Fig. 6). This may be the reason for the generally higher *TY* and apparent *GY* values observed after short-wavelength excitation compared with irradiation through a glass filter (Table I).

Second, UV light absorption by the initiator is necessary for grafting but has a filter effect at the same time. The depth of modification is governed by the penetration depth of excitation light into the
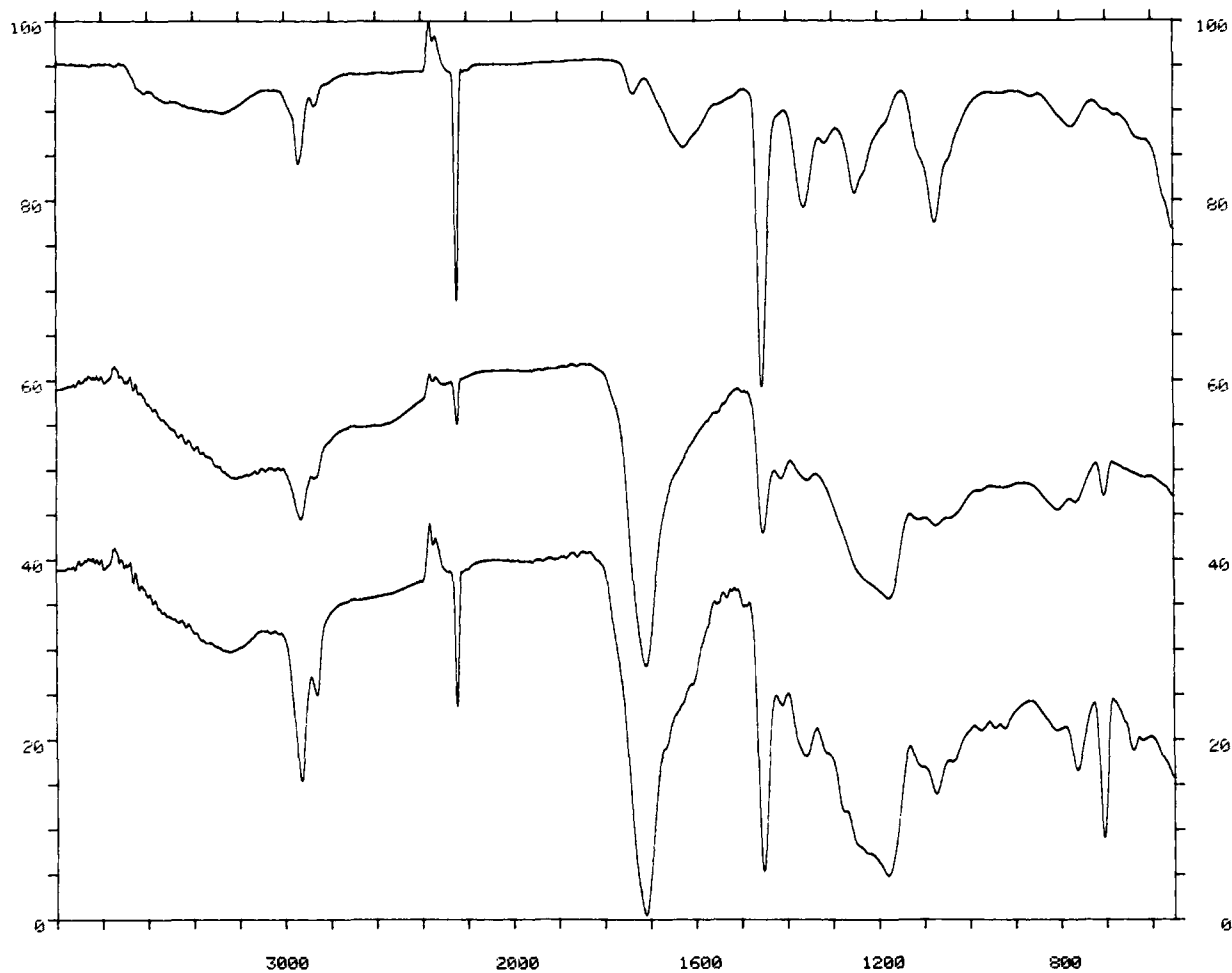

Figure 7 FTIR–ATR spectra of active surface of PAN UF membranes (KRS 5, 45 degree): (a) parent sample; (b) after coating with BP (300 μmol/g) and 60 min UV irradiation (λ_{exc} > 320 nm) in AA atmosphere; (c) same as (b), after extraction—PAN-gr-AA.
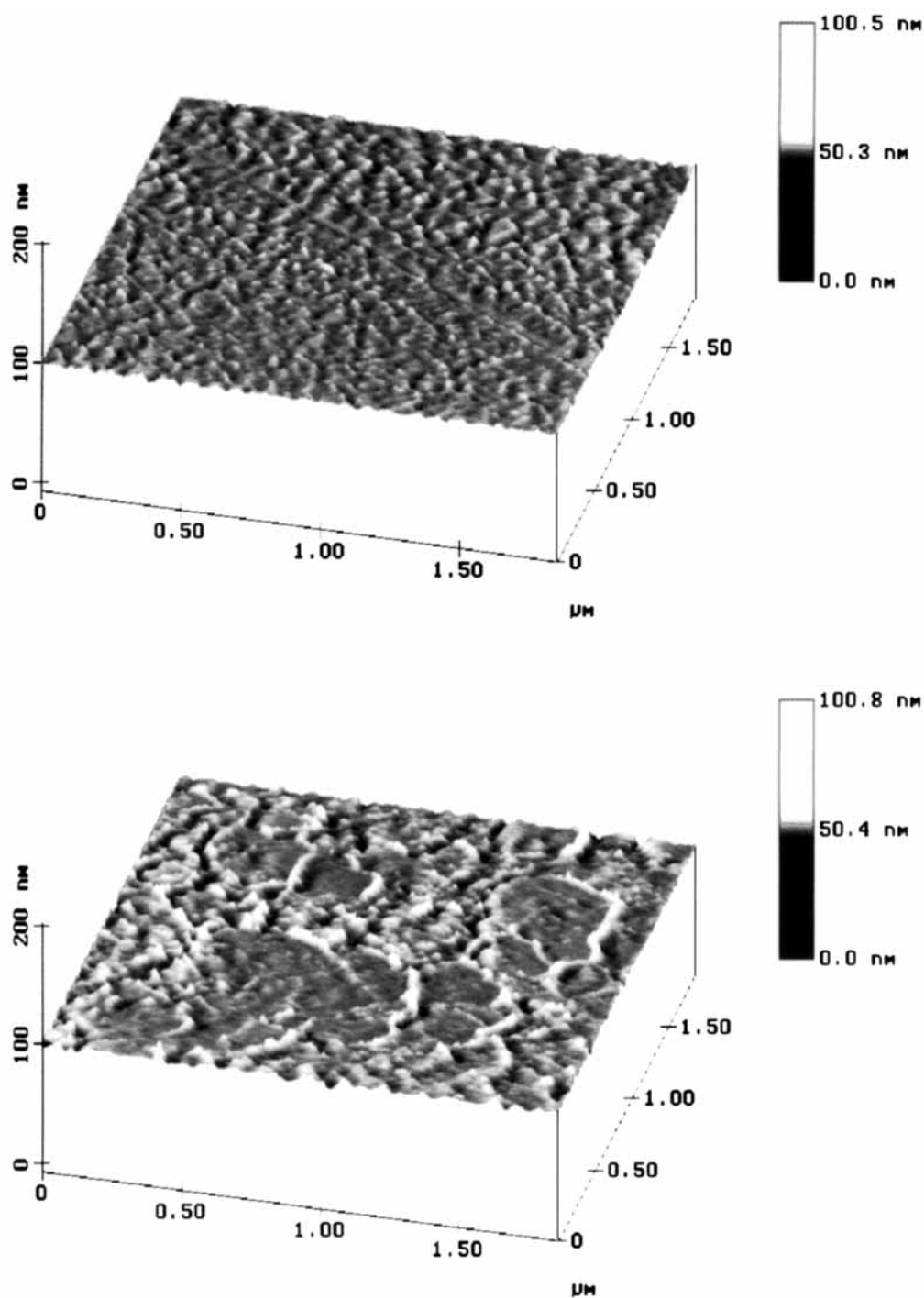
Figure 8   AFM analyses of active surface of PAN UF membranes: (a) parent sample; (b) same as (a), after coating with BP (300 μmol/g), 60 min UV irradiation ($\lambda_{exc} > 320$ nm) in AA atmosphere and extraction—PAN-*gr*-AA surface morphology; (c) preparation as in (b), but before extraction: the lower right sector of the sampled region was covered with a mask during irradiation.
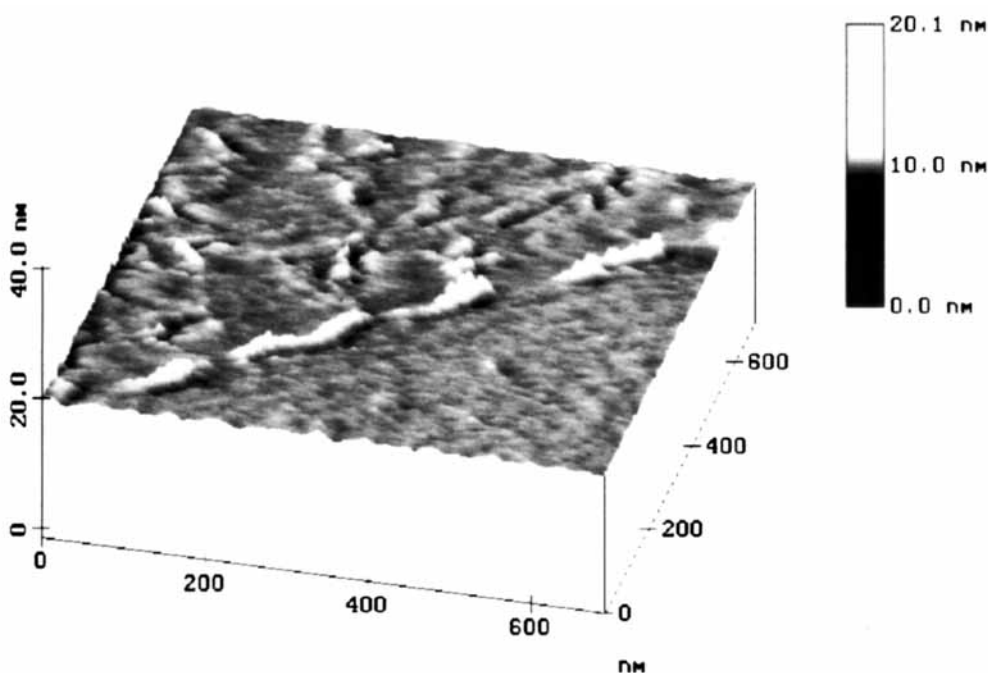
Figure 8   (*Continued from previous page*)

BP-coated membrane matrix; consequently a highly surface-selective modification can be realized (Fig. 9; also confirmed by FTIR-ATR). This is completely different from the UV irradiation-induced (via peroxides) grafting of methacrylic acid onto polyethylene membranes having low intrinsic light absorption, where modification throughout the pore structure is obtained.[39]

Third, regarding the initiation mechanism, formation of PAN radicals due to H abstraction after BP photoexcitation is obviously involved, because PAN functionalization with aromatic groups derived
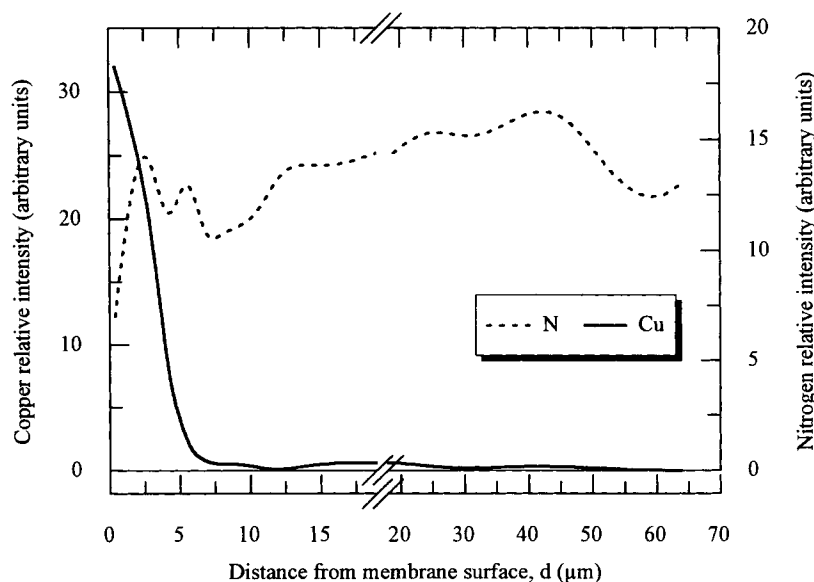

Figure 9   Results from a SEM/EDX mapping analysis of the cross-section of a PAN-*gr*-AA UF membrane (*GY* 1.5%) in copper salt form (total membrane thickness 110 μm): Cu is detected predominately in the top-layer region, demonstrating the surface selectivity of photo graft polymerization modification.

from BP is observed (cf. Figs. 3 and 7). In the presence of monomer AA, a competition between radical recombination (yielding functionalization), and monomer addition (starting graft polymerization) occurs. The reduced functionalization yield in the presence of AA—detected indirectly with HPLC analyses of extracts—is an argument to support this hypothesis.

Fourth, relatively high overall polymerization and graft yields can be realized. On the other hand, a rough quantitative estimate is that with 294 μmol/ g BP loading under the same conditions, up to 100 μmol/g conversion of BP to functionalization products (HPLC results) and 150 to 1,500 μmol/g PAA formation are obtained (for 60 min UV: GY = 4.2 or 1.1% (=580 or 150 μmol/g), TY = 11.0 or 10.0% (=1530 or 1390 μmol/g) for λ_{exc} > 220 and 320 nm, respectively; cf. Table I). This indicates a low overall efficiency of the polymerization process. The average molecular weights of homo-PAA—estimated from GPC results—are between 20,000 and 60,000 g/mol (cf. Fig. 6). Using the assumption that the conditions for chain growth are similar for graft and homopolymer during the grafting step (cf. Uchida et al.[40]), about the same values may be expected for the graft polymer. Hence the efficiency of initiation versus that of polymerization seems to be low. Consequently, relatively low graft density per surface area may be expected.

Fifth, the comparatively high homopolymer yields—unexpected for gas phase photo-grafting— can be interpreted as an indication for initiator mobility. During the comparatively long grafting time, BP may diffuse into the newly formed polymer phase which will contain dissolved monomer AA, there too initiating homopolymerization. Of course, a probable side effect is graft polymerization onto previously formed gr-PAA and homo-PAA (cf. Ogiwara et al.[13]). The increasing width of molecular weight distribution with BP loading (Fig. 6.1) supports these considerations.

Sixth, looking at the influence of the main modification parameters, the grafting rate is decreasing with *time* (Fig. 4). This is expected for a surface reaction. The ratio between graft and homopolymer is lower with enhanced *BP loading* (Fig. 5; cf. Fig. 4). This is obviously due to the fact that graft polymerization is initiated basically by adsorbed BP or by BP close to the surface (for low total BP loading, the percentage of adsorbed BP was estimated as 40%, cf. above). The percentage of "mobile" (not adsorbed) initiator increases with higher loading, also the driving force for diffusion into the newly formed polymer film (cf. above).

Ultrafiltration Properties of PAN-gr-AA UF Membranes

The ultimate aim of our studies is—via photo graft polymerization—to modify the separation performance of UF membranes. Pure water permeability, and ultrafiltration flux and solute retention with dextrane as the standard macromolecule have been measured; results are summarized in Figure 10. Long-wavelength UV irradiation of parent and of BP-coated PAN UF membranes did not significantly change the pure water fluxes and the dextrane separation behavior. For PAN-gr-AA UF membranes there is a clear tendency for the permeability to decrease with increasing PAA graft yield (Fig. 10[a]; $J_{w,o}$ = 300 ± 55 L/m²h at 0.2 MPa). Two groups of data can be distinguished; the same amount of graft polymer produced with UV irradiation through a glass filter (λ_{exc} > 320 nm) has less impact on permeability than PAA produced during short-wavelength excitation (λ_{exc} > 220 nm). For dextrane retention R (R = 46 ± 20% for parent membranes), a steady increase with PAA GY is observed with the tendency to level off at R values beyond 80% for high GYs (Fig. 10[b]).

For several PAN-gr-AA UF membrane types, having different GYs and prepared using short and long wavelength irradiation, the pressure dependency of flux was measured; representative results are shown in Figure 11. For membranes with low GY (< 1%), no significant effect of pressure (in the studied range) on permeability was found. PAN-gr-AA UF membranes with higher graft yields showed a more or less pronounced increase in permeability with enhanced pressure, but a clear difference was seen between samples prepared by irradiation with (λ_{exc} > 320 nm) or without a glass filter (λ_{exc} > 220 nm). A higher susceptibility toward pressure increase causing higher flux was observed for samples prepared by long wavelength, BP selective excitation.

All membrane characterization results can be interpreted as follows: The lack of any UV irradiation effect without the presence of monomer, and the steady decrease of permeability with increasing graft yield GY, demonstrate that the active membrane surface is modified predominately by graft polymer (Fig. 10[a]). Increasing GY seems to reduce average surface pore size (and/or porosity), also causing higher retention of the macromolecular probe dextrane (Fig. 10[b]). This is reasonable considering the location of the grafted polymer exclusively in the surface region (cf. Fig. 9) and the comparatively high M_w estimated for gr-PAA from GPC results of
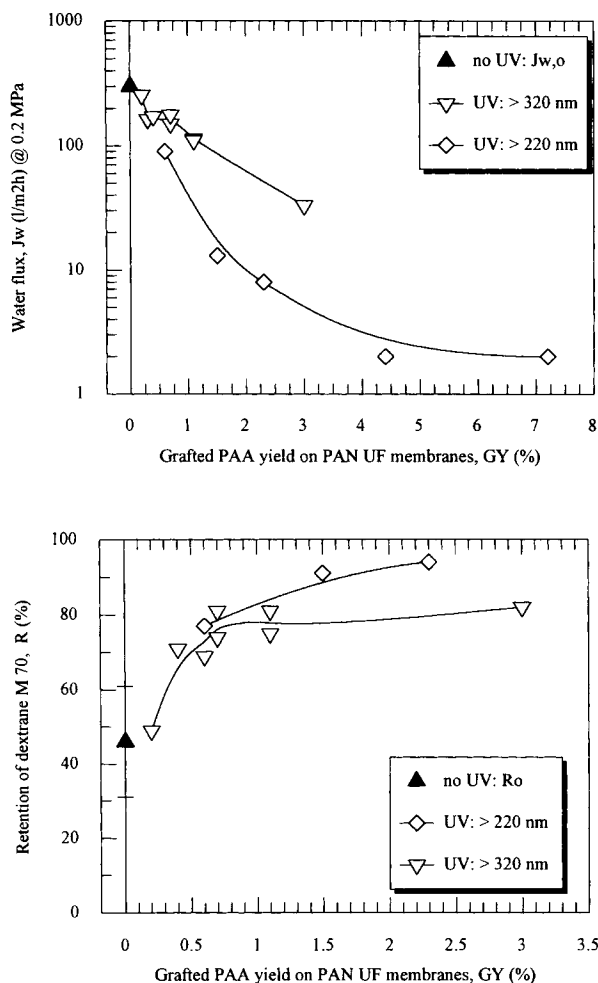
high M_w (long chains; cf. above) may be the precondition for such flexibility. The effect is more pronounced for higher GYs (greater contribution of gr-PAA to total membrane resistance) and depends on graft polymer structure, namely, similar amounts of degraded/crosslinked PAA are not deformable to the same extent as gr-PAA prepared under BP-selective excitation graft conditions.

CONCLUSIONS

Using photo graft polymerization of acrylic acid from the gas phase, a defined chemical modification of the outer surface layer of polyacrylonitrile ultrafiltration membranes is possible. This is demonstrated with various surface analytical methods. A major advantage in the present study is the stability of the substrate—the PAN membrane pore structure—under UV excitation and graft reaction conditions, along with the photoactivation by benzophenone. This is an advantage in comparison with other membrane materials such as polysulfone, where photodegradation of the UF pore structure dominates.[23] Activation without irreversible structure change is possible by soaking with initiator solution; BP loading of the membranes can be varied. The monomer AA can easily be applied from the gas phase, and yields considerable amounts of graft polymer. Concentration variation is possible, e.g.,
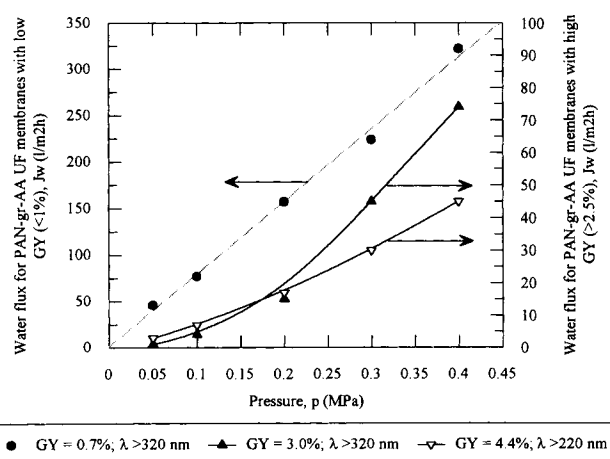
Figure 10 UF performance of PAN-gr-AA UF membranes dependent on PAA graft yields GY; (a): pure water fluxes J_w for samples prepared using long wavelength and short wavelength UV irradiation; (b): retention R for dextrane M70.

homo-PAA (cf. above). However, the differences between samples prepared by selective ($\lambda_{exc} > 320$ nm) and by nonselective UV excitation ($\lambda_{exc} > 220$ nm) lead to the conclusion that graft polymer structure (the degree of degradation and/or crosslinking) has an additional effect on permeability. At the same pressure (0.2 MPa), the permeability of partially degraded/crosslinked PAA on PAN UF membranes is lower than that of the same amount of gr-PAA prepared under selective BP excitation graft polymerization conditions (Fig. 10[a]). The effect of pressure on permeability can be interpreted as shear-induced thinning of a flexible polymer layer—attached to and covering pore walls—by enhancing the transmembrane flow rate via increased pressure.[41] Comparatively low graft density along with relatively

Figure 11 Pressure dependence of pure water fluxes J_w through PAN-gr-AA UF membranes, prepared under different UV excitation conditions and having different GYs (for PAN-gr-AA UF membranes with $GY = 0.7\%$ the curve is a linear fit, $r = 0.998$).

via dilution with inert gas or changing temperature. This gas phase procedure can be used with a large variety of monomers (including glycidyl methacrylate[16]); the intended use of less volatile acrylates (such as PEG derivatives; cf. Uchida et al.[40] may require other variants, such as grafting from the liquid phase. In general, the initiation efficiency is limited by the tendency of the primary polymer/ketyl radical pair to undergo recombination, even in the presence of monomer. The complete suppression of dimerization of ketyl radicals is a consequence of their drastically reduced mobility on the solid PAN surface or in the PAA phase, as compared with the situation in solution. The estimated low graft density (accompanied by relatively long graft polymer chains) is the consequence. The twofold function of BP light absorption, polymerization initiation and filter effect, is the precondition of the pronounced modification surface selectivity. On the other hand, due to the application of BP by simple dip-coating, initiator mobility into/in the graft polymer phase is a problem, especially with increasing graft time and yield. Grafting onto graft polymer and the formation of homopolymer initiated by BP cannot be completely suppressed. A more detailed study by our group of the effects of initiator loading and distribution, UV time and intensity, oxygen influence during and after irradiation onto BP/PAN conversion, and implications for graft polymerization modification is currently in progress. Finally, the specificity of the modification as photoinitiated process may enable the creation of patterned surface structures on UF membranes or in modules.

Via photo graft polymerization, and because of the stability of the base material PAN, the pore structure of the UF membranes is influenced in a defined way, namely, graft polymer (via GY) reduces average pore size and/or porosity. Clear dependencies of GY on modification parameters such as BP loading and UV irradiation time exist; hence membrane surface morphology can be controlled. Already comparatively small amounts of graft polymer (GYs around 1%, relative to total membrane weight; equivalent to a surface coverage S of about 0.5 μmol/g, assuming graft polymer modification of the outer membrane surface exclusively) have a major impact on membrane performance (cf. Vigo et al.[42]). Again, the surface-selective character of the modification is obvious. The photoinitiated process may successfully compete, e.g., with plasma-induced surface selective modifications of UF membranes.[42-44] The generation of desired specific surface properties with additional impact on membrane performance (be-

sides UF selectivity) is possible. Targets are hydrophilicity (e.g., with effect on protein fouling, cf. Nilsson[2]), environment sensitive swelling (e.g., for membrane "switches," cf. Iwata and Matsuda[43] and Iwata et al.[44]) or reactivity (e.g., for covalent immobilization of enzymes[28]). Using various monomers and different variants of the photo graft polymerization modification approach, the evaluation of these possibilities is underway by our group.

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