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Eizo Oikawa; Ken-Ya Watanabe; Toshiki Aoki

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PREPARATION OF GRAFT COPOLYMERS BY MEANS OF UV PHOTOLYSIS OF POLY(METHYL VINYL KETONE) AND REVERSE OSMOSIS PERFORMANCE OF THE MEMBRANES FROM THE OXIMES OF THE COPOLYMERS

EIZO OIKAWA,* KEN-YA WATANABE, and TOSHIKI AOKI

Faculty of Engineering
Niigata University
Niigata 950-21 Japan

ABSTRACT

An attempt was made to prepare a graft copolymer consisting of poly(methyl vinyl ketone) (PMVK) as a backbone chain and polyacrylonitrile, poly(4-vinylpyridine), or polystyrene as a graft chain by UV irradiation of a solution of PMVK in the presence of acrylonitrile, 4-vinylpyridine, or styrene. The influence of reaction conditions on the yield, composition, and viscosity of the resulting graft copolymers was investigated. It was suggested from NMR and gel permeation chromatography that those graft copolymers contained a high molecular weight fraction of narrow distribution and block copolymers as well. The reverse osmosis membranes derived from the oxime and amidoxime of the graft copolymers showed a characteristic performance of exhibiting a maximal difference between rejections against NaCl and CoCl_2 at a certain addition ratio of crosslinking agent, which was not observed in the membranes from copolymers by conventional radical copolymerization. The relationship between these phenomena and the branching structure of the graft copolymers was discussed.

INTRODUCTION

In previous papers we reported that oxime group-containing copolymers and amidoxime group-containing copolymers, which were derived from 4-vinylpyridine (4VP)-methyl vinyl ketone (MVK) copolymer and 4VP-acrylonitrile (AN) copolymer, respectively, by reacting with hydroxylamine, could effectively be utilized as membranes or column packings for the separation of metal ions [1, 2]. This effect is largely owing to the hydrophilicity of $-C=N-OH$ groups. Hence, MVK-AN copolymers are anticipated to increase their efficiency in separation use, since both comonomers have precursor groups of $-C=N-OH$ and can be converted into similar groups. Several polymerization methods are available, such as solution, emulsion, and light-induced polymerization, for the preparation of MVK-AN copolymers. We have confirmed that grafting of AN onto PMVK by means of UV photolysis of PMVK is one of the light-induced method which yields a graft copolymer whose viscosity is higher than that of solution copolymerization with a radical initiator. Since a polymer of high molecular weight usually gives tough films, such a graft copolymer has potential value for reverse osmosis membranes. Although UV photolysis of PMVK has been studied extensively [3, 4], the grafting by radicals resulting from the photolysis of PMVK has only been studied kinetically by Guillet and coworkers with AN, methyl methacrylate, or vinyl acetate as a comonomer [5], and no attempt to use other monomers has appeared. Those graft copolymers are of interest as UV degradative polymers as well.

In the present study, the structure of the resulting graft copolymers and its dependence on the kind of solvent, monomer, and starting PMVK was investigated by fractionation, GPC, IR, NMR, and viscosity measurements. The copolymers were converted into oximes and their membrane performance in reverse osmosis was compared with that of the oxime derived from the copolymers by solution or emulsion methods.

EXPERIMENTAL

Polymerization and Copolymerization of MVK

PMVK, the starting material, was prepared by solution polymerization in a sealed ampule and by emulsion polymerization in a three-necked flask under the conditions shown in Table 1. After a given reaction time,

TABLE 1. Preparation of Poly(Methyl Vinyl Ketone) (PMVK)

PMVK code ^a	Solvent ^b	Monomer Concentration, wt%	Initiator (mol% based on monomer)	Temperature, °C	Time, h	Yield, %	$[\eta]^c$
S1	Dioxane	40.0	AIBN (0.25)	80	6	67.0	0.615
S4	Dioxane	40.5	AIBN (0.51)	80	6	67.9	0.282
S5	Dioxane	40.0	AIBN (0.50)	80	6	64.8	0.361
S2	DMF	40.0	AIBN (0.52)	80	6	65.9	0.304
S3	DMF	40.0	AIBN (0.50)	80	8	99.3	0.476
S6	DMSO	45.7	AIBN (0.09)	80	3.5	63.5	0.566
E9	Water	40.1	BPO (0.09), (NH ₄) ₂ Fe(SO ₄) ₂ (0.15)	50	3.5	42.9	1.470
E7	Water	40.0	BPO (0.05), (NH ₄) ₂ Fe(SO ₄) ₂ (0.21)	50	3	62.0	2.800

^aS = solution polymerization, E = emulsion polymerization with sodium pyrophosphate as a stabilizer.

^bDMF = *N,N*-dimethylformamide, DMSO = dimethylsulfoxide.

^cIntrinsic viscosity in DMF at 25°C.

the contents of the ampule were poured in diethyl ether to precipitate PMVK which was reprecipitated from acetone solution. In the emulsion polymerization, the contents were poured into a large amount of water and the precipitated polymer was reprecipitated from acetone or dioxane solution.

Copolymerizations were carried out in a similar manner (SKN and EKN in Table 2). In the solution copolymerization, the copolymer was precipitated in diethyl ether or water and purified by reprecipitation from DMF-ether. The copolymers with AN, formed by emulsion method, were precipitated in a large amount of water and purified by reprecipitation from DMF-ether.

Grafting by UV Irradiation

A given amount of PMVK solution and comonomer was placed in a Pyrex tube. The atmosphere in the tube was replaced by nitrogen and the tube was sealed. The tube was irradiated with a 400-W high pressure UV lamp UVK-400L of Riko Kagaku Sangyo in a water bath thermostated at 30°C. The distance between the outer walls of the tube and lamp was kept at 5 cm and the tube was rotated by an angle of about 90° every 30 min. The light intensity under these conditions was $5.23 \times 10^{-3} \text{ Ms}^{-1}$ as measured by the ferrioxalate method [6]. After a determined time, the resulting copolymer was precipitated by pouring it into diethyl ether and reprecipitating it from DMF-ether. If a DMF-insoluble fraction was formed, it was removed by filtration with glass fiber cloth.

As controls, comonomers were irradiated in the absence of PMVK. The precipitant was methanol for AN, and water for 4VP and styrene (St). The polymers were reprecipitated from DMF solution.

Photolysis of PMVK

Ampules containing a PMVK solution of the same concentration as in the grafting were irradiated. One ampule was taken out at a given time, and the contents were poured into water to precipitate the polymer. The viscosity of the purified samples was measured in DMF solution at 25°C.

Fractional Precipitation

To a 5% DMF solution in a thermostat at 25°C, the precipitant (methanol, acetone, or diethyl ether for AN graft copolymers, and water for

TABLE 2. Preparation of AN-Graft Copolymers (UKN) with UV Irradiation^a and of MVK-AN Copolymers

Code no.	PMVK ^b ($[\eta]^c$)	Solvent ^c	Irradiation time, h	Yield, ^d %	$[\eta]^e$	AN in copolymer, mol% ^f
UKN4	E7 (2.800)	DMF	2	17.8	1.72	—
UKN9	S2 (0.304)	DMF	2	20.3	0.544	36.1
UKN12	E9 (1.470)	DMF	4	32.7	1.050	52.3
UKN10	S2(0.304)	DMF	5	28.7	0.846	62.6
UKN20	S5 (0.361)	DMSO	4	30.9	2.150	57.7
UKN21	S5 (0.361)	DMSO	4	32.7	1.570	52.7
UKN14	S3 (0.476)	DMF + THF	4	14.7	0.356	47.0
UKN16	S4 (0.282)	DMF + EC ^c	4	40.0	0.471	40.6
UKN17	S4 (0.282)	DMF + NM ^c	4	19.9	0.320	22.2
UKN18	S4 (0.282)	DMAc ^c	4	32.4	0.768	50.8
UNI ^g	—	DMF	4	11.0	—	—

(continued)

TABLE 2. Continued

Code no.	PMVK ^b ([η] ^c)	Solvent ^c	Irradiation time, h	Yield, ^d %	[η] ^e	AN in copolymer, mol.% ^f
SKN1 ^h	—	DMSO	(5) ^j	97.0	0.291	44.6
SKN2 ^h	—	DMSO	(6) ^j	87.7	0.208	45.8
EKN2 ⁱ	—	Water	(1.63) ^j	56.6	2.610	66.2
EKN3 ⁱ	—	Water	(1.33) ^j	73.3	2.04	50.3

^aMolar ratio of AN to monomer unit of PMVK was 5 except for UKN4 where the ratio was 10.

^bConcentration of PMVK was kept at 6.5 wt%.

^c1:1 molar mixture when two solvents were used. EC = ethylene cyanohydrin, NM = nitromethane, DMAc = *N,N*-dimethylacetamide.

^dBased on the total weight of PMVK and AN.

^eIn DMF at 25°C.

^fBy Kjeldahl method.

^gAN (20.7 wt%) was UV irradiated in the absence of PMVK at 30°C.

^hPMVK and AN (1:1) were copolymerized with 0.5 mol% AIBN at 80°C.

ⁱPMVK and AN were copolymerized with 0.18 mol% BPO and 0.21 mol% (NH₄)₂Fe(SO₄)₂ using sodium lauryl sulfate as an emulsifier and sodium pyrophosphate as a stabilizer at 50°C.

^jCopolymerization time.

4VP graft copolymers) was slowly added dropwise with stirring. The stirring was continued for some time after the occurrence of the precipitate, and then the precipitate was separated by centrifuging. To the supernatant solution was added a further amount of the precipitant. This operation was repeated until no further precipitation occurred.

Oximation and Amidoximation

To a 50% DMF solution of the polymers was added an excess of hydroxylamine hydrochloride and anhydrous sodium carbonate, and the reaction was continued for 4 h at 75°C as described previously [1].

Reverse Osmosis (RO)

Membrane preparation from a 15% DMSO solution with divinyl sulfone (DVS), a crosslinking agent, and the desalination operation with 0.06 M feed solution under a nitrogen pressure of 80 kg/cm² with a batch apparatus have previously been reported [1]. Salt rejection, R , and hydraulic water permeability, K_1 , were estimated according to

$$R = 100(c - c')/c$$

$$J_v = K_1(\Delta P - \Delta\pi)/\Delta x$$

where c and c' are feed and product concentration, respectively, J_v is the volumetric flux, ΔP is the pressure difference, $\Delta\pi$ is the osmotic pressure difference between the feed and product solution, and Δx is the membrane thickness.

Measurements

¹H-NMR spectra were recorded in DMSO-*d*₆ with a JEOL JNM-PMX60, and IR spectra of films with a Hitachi IR spectrophotometer type 270-30. GPC was conducted in a 0.2% DMF-THF (1 : 1 in volume) solution with a Hitachi GPC-655A-11. The column used was a GL-S300MDT-5, and detection was made by differentiating the refractive index.

Tensile strength of membranes was measured with a TOM-5 instrument of Minebea Co. and expressed as the relative strength compared with the strength of a cellulose acetate membrane [7]. The water content is the weight fraction of water in a wet membrane [1].

RESULTS AND DISCUSSION

Preparation of AN Graft Copolymers

In the photodegradation of PMVK the dependence of the relative intrinsic viscosity on irradiation time is shown in Fig. 1. Apparently, scission of the polymer chain occurred, which corresponds to Norrish II type in Scheme 1 [5]. The degradation in DMF was more pronounced than in DMSO, and the higher the viscosity of the starting polymer, the more pronounced the degradation.

Table 2 shows the results of UV irradiation on PMVK solutions in the presence of AN. PMVK materials with a lower viscosity, such as S2-5, yielded graft copolymers of higher viscosity in general, suggesting the occurrence of graft copolymer. On the other hand, PMVKs of higher

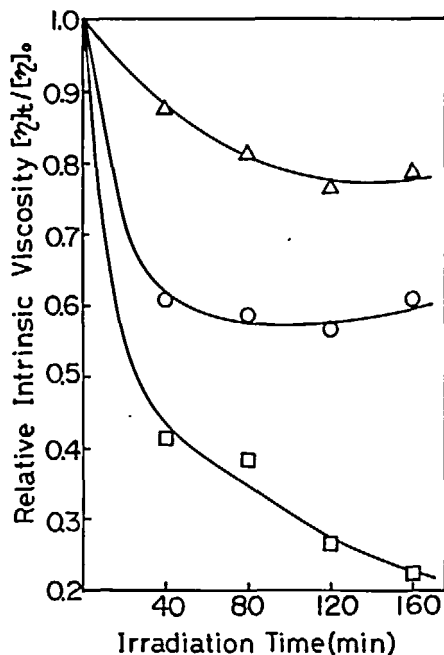
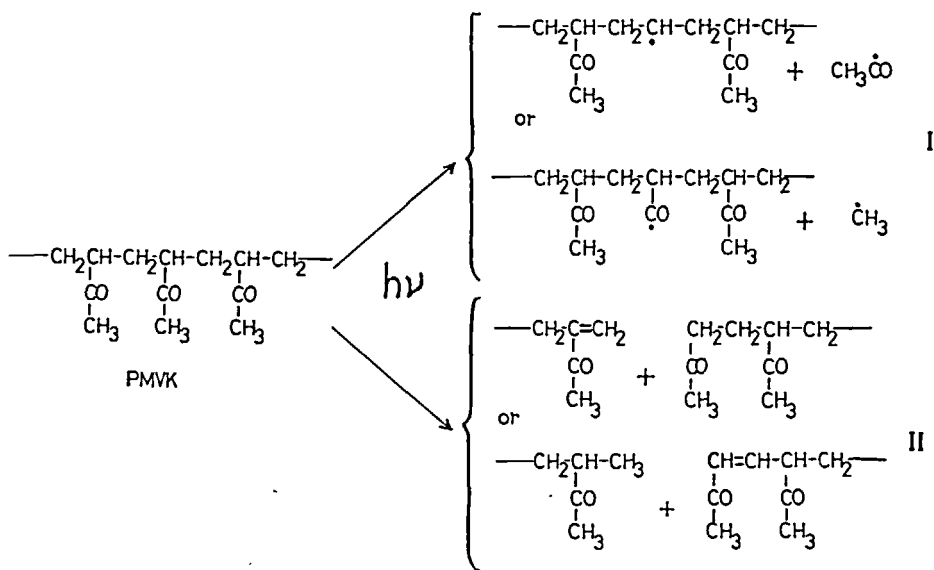


FIG. 1. Change in relative intrinsic viscosity of PMVK with irradiation time. (○) S1 ($[\eta]_0 = 0.615$) in DMF, (□) E7 ($[\eta]_0 = 2.800$) in DMF, (△) S6 ($[\eta]_0 = 0.566$) in DMSO.



SCHEME 1. Photodegradation of PMVK.

viscosity, such as E7-9, formed graft copolymers of lower viscosity, indicating more pronounced degradation of the chain. However, incorporation of AN into the polymer chain was confirmed by $\text{C}\equiv\text{N}$ absorption in the IR spectra. Yield, viscosity, and AN content tended to increase with an increase in irradiation time (UKN9 vs UKN10). It was found from the addition of AN in various ratios to the charged PMVK (e.g., UKN4 and UKN12) that a larger amount of AN did not increase the yield, and the optimum ratio was 5 under the conditions of Table 2.

The solvents used include aprotic ones like DMF, DMSO, and DMAc; cosolvents like EC and NM capable of solvating polyacrylonitrile (PAN) [8]; and THF (UKN14-17). THF did not yield any precipitate, but it did reduce the yield and viscosity of the resulting copolymer. This could be ascribed to photooxidation of THF by traces of air into a peroxide which in turn consumed radicals. EC gave a transparent and gel-like deposit on the inner ampule wall, which amounted to 40% of the total copolymer, showing a low solubility to the copolymer. NM reduced the yield and particularly the AN content. This is attributable largely to a high chain transfer constant C_t of NM (C_t at 60°C : 10×10^{-4} for St, 2300×10^{-4} for

vinyl acetate [9]). The reaction proceeded homogeneously in aprotic solvents except for DMAc where a small amount of turbidity was observed, probably because of low solubility. Accordingly, DMF and DMSO were good solvents for the reaction, particularly DMSO, because of less chain scission as shown in Fig. 1 and the formation of copolymers of higher molecular weight (Table 2). The difference between DMF and DMSO appears to result from the difference in chain transfer ($C_s(\text{DMF}) = 4 \times 10^{-4}$, $C_s(\text{DMSO}) = 0.48 \times 10^{-4}$ for St at 60°C ; $C_s(\text{DMF}) = 2.78 \times 10^{-4}$, $C_s(\text{DMSO}) = 0.29 \times 10^{-4}$ for AN at 50°C [9]).

Structure of the Resulting Copolymers

The AN content of the copolymers was calculated assuming that all AN polymerized was incorporated in PMVK, but it is possible to simultaneously yield AN homopolymer by AN radicals formed by chain transfer or direct transfer of UV energy to AN. Therefore, the influence of UV light on the monomer AN in the absence of PMVK was investigated. The results were isolation of PAN in 11% yield (UN1 in Table 2). The resulting copolymers were subjected to fractional precipitation in order to check whether PAN was formed (UKN4 in Table 3). PAN in the polymer mixture may precipitate in the initial stage upon the addition of precipitant. The results in Table 3 reveal that the polymer of highest AN content tended to precipitate initially with the addition of methanol with no significant change in viscosities of the fractions, but with the addition of acetone and ether, both AN content and viscosity showed a tendency to decrease. Even with the addition of acetone which can dissolve PMVK, the first fraction showed a distinct and deep IR absorption at 1714 cm^{-1} due to C=O stretching. This absorption was larger than that of nitrile at 2244 cm^{-1} , as is shown in Table 3, and this fact clearly indicates the incorporation of MVK into the first fraction. Although very slow addition of the precipitant was carried out in order to form the first precipitate in as small an amount as possible, a considerable amount of gel-like precipitate was always formed at the first precipitation. All these facts indicate the absence of PAN under these reaction conditions. This can be accounted for by facile hydrogen abstraction from the tertiary carbon of PAN, followed by incorporation of PAN into PMVK.

As shown in Scheme 1, scission is possible not only in side groups but also in the backbone, and Fig. 1 demonstrates that the latter scission took place. The resulting polymer fractions containing terminal double bonds can readily react with radicals and may lead to the formation of branches

TABLE 3. Fractionation of UKN4 and UK4V6

Polymer code	Fraction		$[\eta]^a$	AN or 4VP mol%	A_{1714}^b
	No.	wt%			A_{2244}
UKN4 ^c	1	52	1.760	56.9	3.59
	2	12	1.806	51.6	7.58
	3	6	—	49.3	5.88
	4	2	—	—	—
	5	12	1.590	33.6	16.78
UKN4	1 ^d	33.3	1.905	66.7	5.15
	2 ^e	55.0	1.593	37.2	3.21
	3 ^e	10.0	1.273	28.0	4.60
UK4V6 ^f	1	0.08	—	—	—
	2	1.2	—	49.2	—
	3	59.6	0.986	55.1	—
	4	7.3	0.619	94.4	—
	5	18.5	0.800	82.1	—
	6	2.7	—	85.4	—

^aIn DMF at 25°C.

^bAbsorbance ratio in IR spectra at 1714 and 2244 cm⁻¹.

^cAll fractions were precipitated with methanol.

^dPrecipitated with acetone.

^ePrecipitated with diethyl ether.

^fAll fractions were precipitated with water.

or a block copolymer if chain transfer accompanied with termination occurs.

The GPC curve of UKN12 in Fig. 2 is conspicuous due to its sharp peak of narrow distribution at a higher molecular weight than that of the starting PMVK-E9, together with a smaller broad peak at lower molecular weight. The existence of a low molecular weight fraction may be responsible for the lower intrinsic viscosity of UKN12 than of E9. The peak at a lower molecular weight in the two peaks of E9 may represent PMVK derived from water-soluble MVK in a homogeneous phase where termination is prone to occur. The existence of a higher molecular weight fraction of narrow distribution in UKN12 is consistent with the tendency of the first fraction to precipitate in a large amount.

Grafting with 4VP or St

An attempt was made to prepare a graft copolymer with 4VP by a similar method of UV irradiation, since we have reported the membrane performance of the oxime of 4VP-MVK copolymer obtained by solution copolymerization with radical initiator [1]. The results are tabulated in Table 4 (UK4V) which shows lower yields in general than with AN, higher viscosities, and considerable 4VP contents. As shown in U4VP1, 4VP yielded only a small amount of its homopolymer by UV irradiation, suggesting that most of the 4VP was incorporated into PMVK to yield the

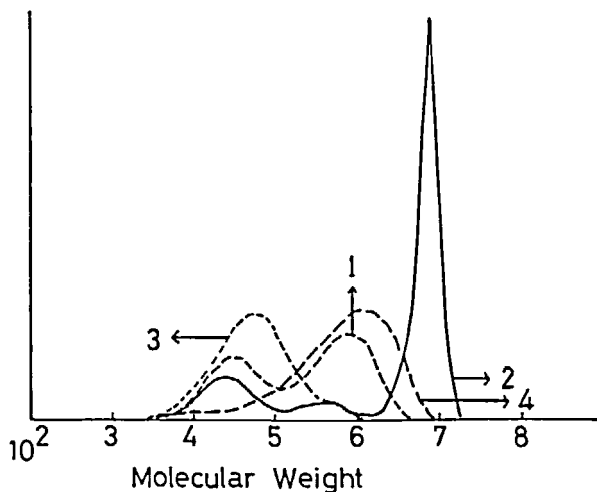


FIG. 2. GPC curves of (1) PMVK-E9, (2) UKN12, (3) SKN1, (4) EKN2.

TABLE 4. Preparation of 4VP Graft Copolymers (UK4V) with UV Irradiation^a and of MVK-4VP Copolymers.

Code no.	[4VP]/ [MVK unit of PMVK]	Solvent	Yield, ^b %	[η] ^c	4VP in copolymer, mol% ^d
UK4V4	8.00	DMSO	9.1	0.595	48.6
UK4V3	5.04	DMSO	26.1	0.700	48.1
UK4V6	5.03	DMSO	19.5	1.050	65.7
UK4V7	5.00	DMSO	18.8	0.711	51.1
UK4V1	5.00	DMF	13.9	0.949	26.0
UK4V2	5.00	DMF	11.3	0.484	20.9
U4VP1 ^c	—	DMSO	1.7	—	—
SK4V1 ^f	—	DMSO	62.5	1.270	57.6
SK4V3 ^f	—	DMSO	82.0	0.908	48.1
SK4V4 ^f	—	Dioxane	63.0	0.498	48.3

^aPMVK S5 ($[\eta] = 0.361$) was used at a concentration of 6.5 wt%. Irradiation time: 4 h.

^bBased on the total weight of PMVK and 4VP on grafting.

^cIN DMF at 25°C.

^dDetermined by ¹H-NMR.

^e4VP (34.3 wt%) was UV-irradiated in the absence of PMVK at 30°C for 4 h.

^fMVK and 4VP (~1 : 1, 60 wt%) were copolymerized with 0.1–0.25 mol% AIBN at 75–80°C for 4–6 h.

copolymer products UK4V listed in Table 4. An excessive amount of 4VP was not effective (UK4V4) in increasing the yield, similar to the case of AN. DMSO gave better results than DMF in yield and 4VP content, probably due to the lower chain transfer constant of DMSO. The results of fractionation of the copolymer (UK4V6) are shown in Table 3. High contents of 4VP were found in intermediate fractions, and they represent a pronounced difference from AN grafting. This can be attributed to the

small extent of chain transfer of 4VP. This contrasts with the results of AN and supports the facility of AN to transfer, resulting in no isolation of PAN.

For St, which has an aromatic ring similar to 4VP, the results are summarized in Table 5. Yields were very low and were not improved even with a twofold concentration increase of PMVK as with AN. This is consistent in that no PSt was obtained at a high concentration of St either (USt1).

Of these three monomers, AN most readily produced the copolymer, and the decreasing order of copolymer formation was AN, 4VP, and St. This order coincides with that of the resonance stabilization of the monomers as shown in Q values; $Q(\text{AN}) = 0.60$, $Q(4\text{VP}) = 0.82$, and $Q(\text{St}) = 1.0$ [10].

RO Performance of the Membrane of the Copolymer Oximes

(a) Crosslinking in Membrane Preparation

Complete oximation and amidoximation of samples were confirmed by the disappearance of IR absorptions at 1714 cm^{-1} due to $\text{C}=\text{O}$ and

TABLE 5. Preparation of St Graft Copolymers (UKSt) with UV Irradiation^a

Code no.	[St]/[MK unit of PMVK]	Solvent	Concentration of PMVK, wt %	Yield, ^b %
UKSt1	5.04	DMF	6.4	5.2
UKSt2	5.07	DMSO	6.4	7.6
UKSt3	5.46	DMF	12.1	10.8
UKSt4	5.02	DMSO	11.8	9.2
USt1 ^c	—	DMSO	—	1.7

^aPMVK S5 ($[\eta] = 0.361$) was used. Irradiation time: 4 h.

^bBased on the total weight of PMVK and St.

^cSt (51.6 wt %) was UV-irradiated in the absence of PMVK at 30°C for 4 h.

2244 cm^{-1} due to $\text{C}\equiv\text{N}$ stretching. These oximated samples hereafter carry "X" at the end of their code numbers.

An effective crosslinking reaction with DVS could be observed by the termination of rising bubbles; that is, on heating at 80°C after the addition of 15 mol% (based on $-\text{C}=\text{N}-\text{OH}$) DVS to a 8-wt% DMSO solution of EKN3X, air bubbles blown into the bottom of the flask stopped moving at 8 min after the content gelled. For SK4V4X, a 15-wt% solution gradually turned viscous after 70 min and then increased in viscosity until the bubbles stopped at 4 h. In membrane preparation, solvent evaporation increases the concentration and the reaction velocity. Since membranes of 4VP-MVK copolymer oxime [1] and 4VP-AN copolymer amidoxime [2] were prepared at 80°C by 2 h drying from 15 wt% DMSO solution, the same drying conditions were used throughout this work.

(b) Comparison between Oximes of AN Graft Copolymer by UV Irradiation and MVK-AN Copolymer by Emulsion Method

Figure 3 shows the dependence of salt rejection (R), hydraulic water permeability (K), relative strength, and water content (cf. Experimental Section) on the addition ratio of DVS for NaCl and CoCl_2 feeds. Outstanding in Fig. 3 is the extreme lowering of R against NaCl at a 25-mol% addition of DVS in UKN20X. Two repeat experiments of DVS addition around 25 mol% were conducted, and the rejections were found to be $R(\text{NaCl}) = 47.1, 55.0\%$; $R(\text{CoCl}_2) = 99.1, 93.7\%$. The results shown in Fig. 3 were the best found. This behavior seems to be characteristic of graft copolymers, since a similar tendency for UKN12X is observed in Fig. 4 and no similar tendency for EKN3X is observed. The resulting graft copolymers are supposed to have a considerable degree of branched structure as compared with copolymers formed by a conventional radical method. It is a common phenomenon that intermolecular distance is reduced on crosslinking and membranes shrink to some extent. Upon the addition of a small amount of DVS, contraction can be attained by the movement of the noncrosslinked flexible parts of the membrane matrix, but with the addition of a certain ratio of DVS likely results in voids of molecular size by pulling the polymer chains toward each other upon shrinking. They also create large immobile rings because of their branched structure. These actions permit salt to penetrate and they lower the R value. Further addition of DVS gives rise to DVS's whose two unsaturated groups are not entirely employed in crosslinking. The

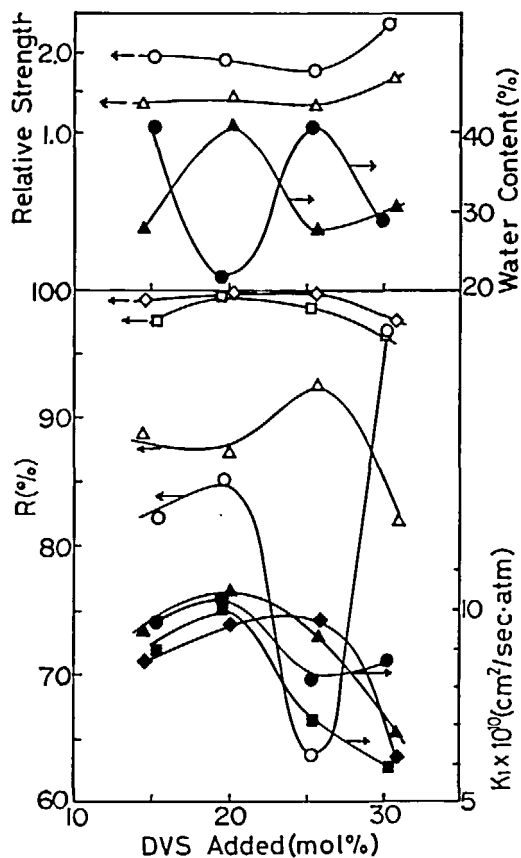


FIG. 3. RO performance of membranes prepared from the oximes of AN graft copolymer (UKN20) and MVK-AN copolymer by emulsion method (EKN3) vs DVS added. (Mol% is based on $-C=N-OH$. Symbols for relative strength and water content are irrelevant to solute.)

	NaCl	CoCl ₂	$[\eta]$	AN, mol%
UKN20	○ ●	□ ■	2.15	57.7
EKN3	△ ▲	◇ ◆	2.04	50.3

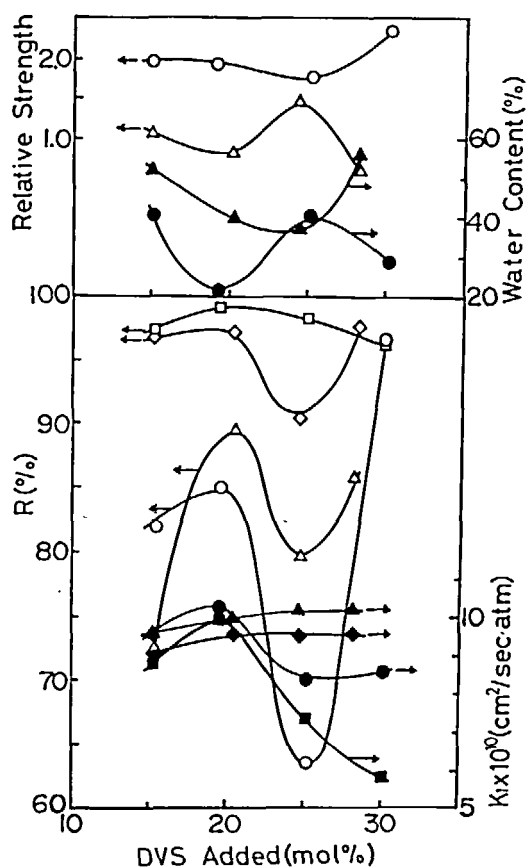


FIG. 4. RO performance of membranes prepared from the oximes of AN graft copolymers of different viscosity vs DVS added (cf. Fig. 3).

	NaCl	CoCl ₂	[η]	AN, mol%
UKN20	○ ●	□ ■	2.15	57.7
UKN12	△ ▲	◇ ◆	1.05	52.3

polymer molecules that contain such DVS could move and play a role in covering regions of low polymer chain density [1]. A maximal increase in water content at 25% DVS indicates the existence of voids of molecular size. The absence of a decrease in R against CoCl_2 is explained in terms of the complexation of CoCl_2 with the membrane material and swelling of the complex.

No extreme change in R was seen in EKN3X. This may be because the original linear structure of EKN3X, in which molecules are mobile and flexible compared with UKN, do not form voids on shrinking.

Because of its branched structure, UKN had an optimum ratio of DVS addition at which the difference in R between NaCl and CoCl_2 was maximal. This membrane was about twice as strong as the cellulose acetate membrane and could be used for the separation of the two salts.

(c) Dependence on the Molecular Weight of UKN Copolymers

Figure 4 shows the membrane performance of UKN20X and UKN12X. The composition of the two copolymers is somewhat different but the viscosity of the copolymers before oxidation is considerably different. UKN12X shows a minimum of $R(\text{NaCl})$ at about 25 mol% DVS, as does UKN20X. The higher values of $R(\text{NaCl})$ in UKN12X of lower molecular weight are probably due to the higher mobility of UKN12X molecules on shrinking by crosslinking, resulting in membranes containing fewer voids. The relative strengths indicate that a polymer with a longer chain length is more favorable for the formation of a stronger membrane.

(d) Effect of Comonomer

Figure 5 shows the membrane performance of UKN20X and UK4V7X, both of which were prepared by UV irradiation. UK4V also had a minimal value of $R(\text{NaCl})$ at about 15 mol% DVS, similar to UKN copolymers, which is attributable to its branched structure. K_1 of UKN generally showed higher values. This stems from the difference in hydrophilicity between $-\text{C}(\text{NH}_2)=\text{N}-\text{OH}$ derived from AN and the pyridine rings of 4VP, with the former being more hydrophilic.

The membrane strength of UKN is naturally larger because of a higher crosslinking density at the same molar ratio based on $-\text{C}=\text{N}-\text{OH}$ in the addition of DVS. However, it is apparent that UK4V can give stronger membranes than can cellulose acetate.

The UK4V membrane showed a maximal difference in R between

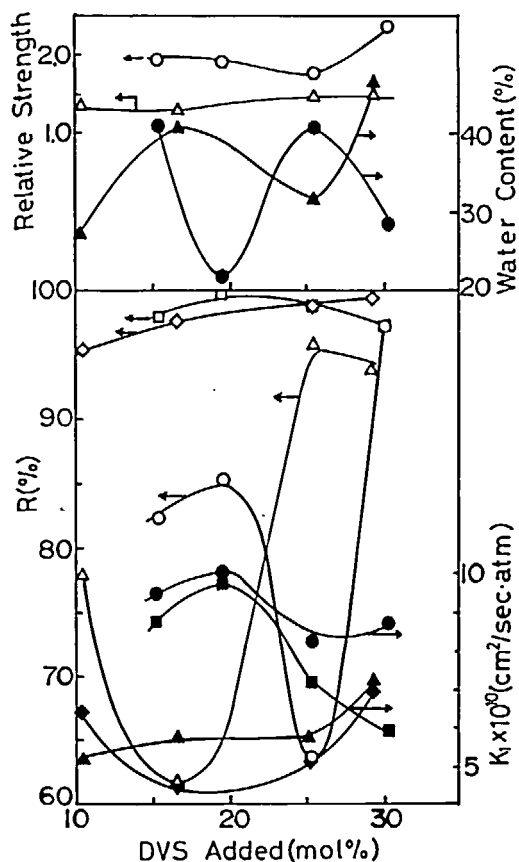


FIG. 5. RO performance of membranes prepared from the oximes of AN and 4VP graft copolymers vs DVS added (cf. Fig. 3).

	NaCl	CoCl ₂	[η]	MVK, mol%
UKN20	○ ●	□ ■	2.15	42.3
UK4V7	△ ▲	◇ ◆	0.711	48.9

NaCl and CoCl_2 at DVS additions of 15–20 mol%, and this membrane can be used for the separation of the two salts.

(e) Comparison between the Oximes of 4VP Graft Copolymer by UV Irradiation and MVK-4VP Copolymer by Conventional Solution Method

The performance of the two copolymer membranes is depicted in Fig. 6. The MVK-4VP copolymer was previously studied [11], and it showed performances very similar to those found in this study without any depression of $R(\text{NaCl})$ at about 15 mol% DVS [11]. UK4V7X, which is of lower viscosity than SK4V3X, showed higher strengths. This may have been caused by effective crosslinking of added DVS in UK4V7X where clustering of $-\text{C}=\text{N}-\text{OH}$ groups is favorable for the nearly complete crosslinking of DVS. On the other hand, the pyridine moieties and $-\text{C}=\text{N}-\text{OH}$ groups in SK4V3X are randomly arranged along the chain and the extent of DVS crosslinking is less than in UK4V7X. Therefore, SK4V3X molecules still have some mobility even after crosslinking. Both mobility and a higher ratio of the remaining $-\text{C}=\text{N}-\text{OH}$ groups can contribute to an increase in K_1 . Water content is not likely to be responsible for the higher K_1 values of SK4V3X than of UK4V7X in view of their similar contents.

CONCLUSION

UV irradiation to PMVK solution in the presence of AN gave a graft copolymer of PMVK which had a high molecular weight fraction of narrow distribution and contained a block structure as well. No polyacrylonitrile was isolated by fractionation. DMSO was the most favorable of the solvents used because of its high solubility and low chain transfer constant. In the grafting of 4VP, a fraction with a high content of 4VP was isolated, probably due to the less frequent chain transfer of 4VP than of AN. Only a very small yield of the graft copolymer was obtained with St. The differences found for different monomers were consistent with differences in their resonance stabilization.

The amidoxime and oxime of the resulting AN and 4VP graft copolymers gave tough membranes after effective crosslinking with DVS. The addition of specific amounts of DVS resulted in maximal difference in rejections between NaCl and CoCl_2 , thereby exhibiting a characteristic different from that in the oximes of the copolymers by radical polymer-

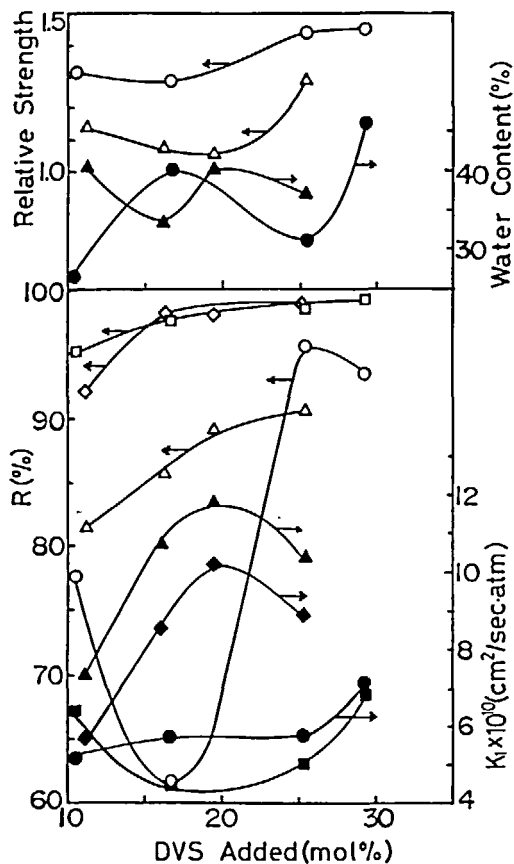


FIG. 6. RO performance of membranes prepared from the oximes of 4VP graft copolymer (UK4V7) and MVK-4VP copolymer by solution method (SK4V3) vs DVS added (cf. Fig. 3).

	NaCl	CoCl ₂	[η]	4VP, mol%
UK4V7	○ ●	□ ■	0.711	51.5
SK4V3	△ ▲	◇ ◆	0.908	48.1

ization. This was attributable to the branched structure of UV-induced graft copolymers and facile crosslinking. The membranes derived from the AN graft copolymer were more water permeable than those from the 4VP graft copolymer because of the higher hydrophilic properties of the former.

REFERENCES

- [1] E. Oikawa, Y. Igarashi, and S. Tsurumaki, *J. Appl. Polym. Sci.*, **30**, 1511 (1985).
- [2] E. Oikawa and S. Tsurumaki, *Ibid.*, **34**, 337 (1987).
- [3] E. Dan and J. E. Guillet, *Macromolecules*, **6**, 230 (1973).
- [4] Y. Namariyama, H. Takao, T. Fujii, and K. Nakamura, *Kobunshi Ronbunshu*, **37**, 261 (1980).
- [5] J. E. Guillet and R. G. W. Norrish, *Proc. Roy. Soc. London, Ser. A*, **233**, 172 (1956).
- [6] C. G. Hatchard and C. A. Parker, *Ibid.*, **235**, 518 (1956).
- [7] E. Oikawa and K. Jindai, *Polym. Bull.*, **16**, 351 (1986).
- [8] M. Kurata, M. Iwama, and K. Kamada, in *Polymer Handbook* (J. Brandrup and E. H. Immergut, eds.), Wiley-Interscience, New York, 1967, p. IV-204.
- [9] J. C. Masson, *Ibid.*, p. II-77.
- [10] L. J. Young, *Ibid.*, p. II-341.
- [11] E. Oikawa and Y. Igarashi, *J. Appl. Polym. Sci.*, **29**, 1723 (1984).

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