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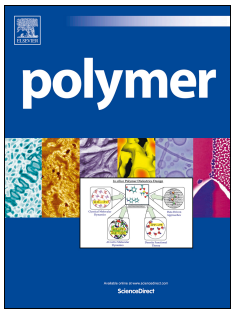

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Graphical Abstract

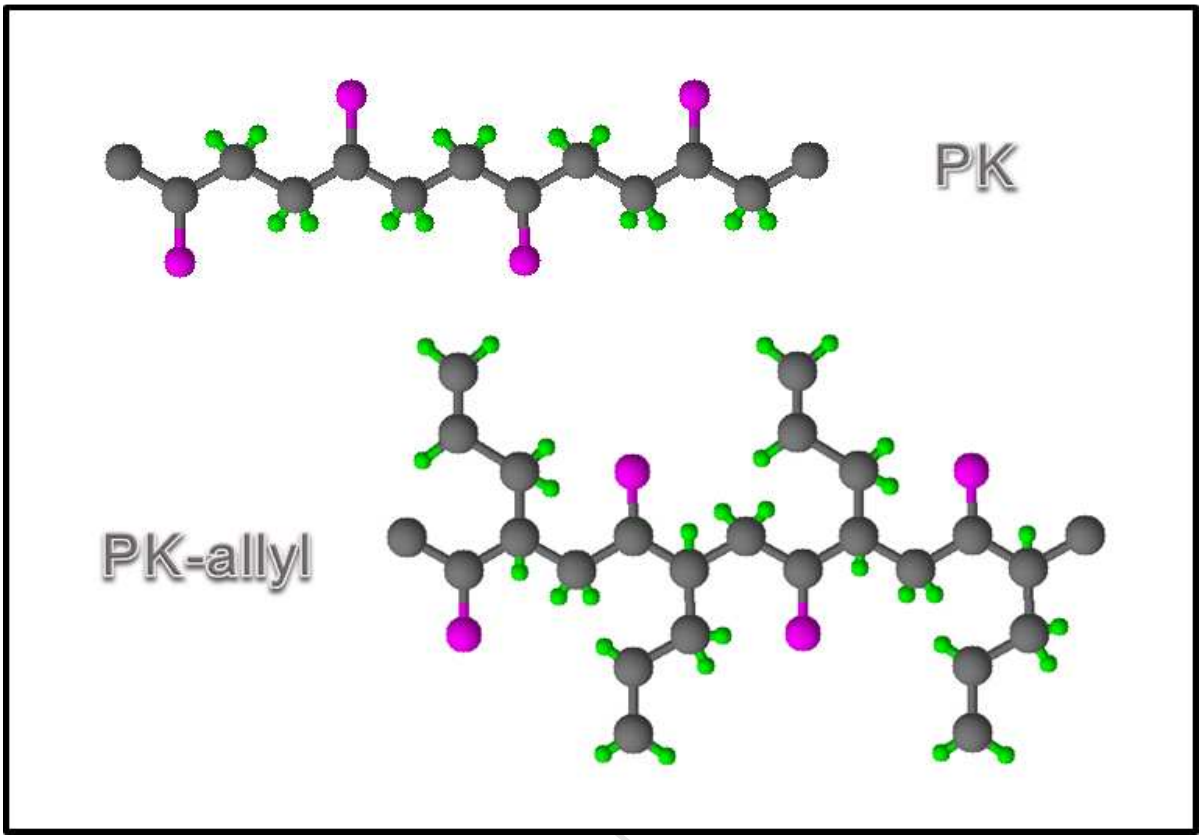

Figure. Grafting pending allyl groups onto polyketone polymer chain.

An Efficient and Facile Method of Grafting Allyl Groups to Chemically Resistant Polyketone Membranes

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ABSTRACT

Polyketone is a thermoplastic polymer known for its strong mechanical properties and chemical resistance. Such superiorities make it difficult to process and chemically modify for further functionalizations and applications. In this work, we introduce a novel method for functionalizing the alpha carbon of polyketone. We succeeded to attach allyl groups to the backbone of polyketone by a heterogeneous reaction between polyketone enolate and allyl bromide. Allylated polyketone is not soluble in common solvents. Since we started with a membrane of polyketone, there is no need to cast again. Further functionalization is possible through pending allyl groups via alkene addition reactions and ionic or radicalic polymerization. FTIR, elemental analysis, solid NMR, FT-Raman, SEM and XPS methods were employed to confirm the elemental composition, molecular structure and morphology. In addition, X-ray diffractometer (XRD), UV-Visible spectroscopy and thermal analysis were used to investigate the crystal structure, physical and electronic properties.

Keywords : Polyketone; potassium *tert*-butoxide; enolization; allyl bromide; grafting

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1. Introduction

Polyketone, which is one of the high performance thermoplastic polymers, is a type of copolymers and terpolymers made of alternating copolymerization of carbon monoxide and ethylene or a mixture with propylene. It is an environmentally friendly polymer making use of carbon monoxide as raw material which is actually a serious air pollutant and toxic gas [1-4]. Due to polar carbonyl group in the main chain, it has a semi-crystalline, occasionally polymorphous, and compact crystal structure, which improves the physico-chemical properties through intramolecular and intermolecular interactions [5,6]. Hence, it demonstrates a useful variety of strong chemical resistance, impact resistance, abrasion resistance and gas barrier properties [7,8].

Initially, the US and Japan companies challenged to commercialize copolymer of polyketone. In 2013, Hyosung Corporation (Korea) became the first in the world to succeed in developing an economically efficient way to deliver copolymer of regularly alternating carbon monoxide and ethylene, and named their product POKETONE. This product is highly promising for thermoplastics applications such as automobile and electronic parts due to its excellent impact resistance, chemical resistance and flame retardancy compared to the conventional engineering plastic nylon. According to Hyosung Corporation's report, POKETONE has a chemical resistance superior to that of nylon by more than 30%, and has higher resistance to chemicals among many other plastic materials. It also has excellent impact resistance compared to PA (polyamide) and PBT, and has excellent impact strength of over 230% compared to Nylon. POKETONE has 14 times better abrasion resistance than polyoxymethylene (POM), and has the advantage of reducing friction noise. Therefore, polyketone can be used for interior and exterior materials in automobile, electric and electronics fields due to aforementioned advantageous characteristics [9].

Researchers have focused on polyketone copolymers composed of other type of monomers [10,11] so far until a convenient method has just recently been invented for synthesis of this type of polyketone. To our knowledge, there is scarce information about chemical functionalization of carbon monoxide and ethylene copolymer since it is rather a new kind. Previously in our group, we used γ-irradiation grafting technique to incorporate functional groups to polyketone chain of POKETONE [12,13]. γ-irradiation can cleave C-H bonds of alpha carbons homolytically, which can perform a radicalic attack towards double bonds of grafting monomers. Vinyl compounds bearing sulfonyl or amine groups were incorporated to polyketone backbone by our group. Only such an energetic

method enabled modifying aliphatic part of the chain. Some researchers used Paal-Knorr reaction to modify carbonyl group of polyketone into pyrrols, then they attached some functional groups to the extension of the pyrrole ring for endowing further functionality [6,14-19]. This method apparently changes the intrinsic chemical and physical properties of polyketone since most carbonyl groups are chemically modified, thus it can't be even called a polyketone anymore. It has been revealed to us that there was not satisfactory amount of work in the literature which deals with chemical modification of polyketone (here we refer as PK anymore) without major changes in main chain atoms. If the chemical modification of PK and monomer grafting can be succeeded in a controlled manner, incorporation of charged functional groups to PK chain will be feasible for manufacturing ion exchange membranes which preserve highly advantageous mechanical properties of polyketone backbone adequately. Such engineered membranes derived from PK may be promising for the design of tenacious membranes for long-term use in water treatment [20-23], energy applications, e.g. redox flow batteries [24-28], and material separations [29-31] etc.

Here we introduce a new method which exploits alpha carbon chemistry of carbonyl compounds. A strong base such as potassium *tert*-butoxide (KO*t*Bu) can easily remove relatively acidic hydrogen of alpha carbon [32-34]. Among negatively charged resonance forms of enolate, carbanion form can bind electropositive centers with strong C-C bonds. We used allyl bromide to attach allyl groups to the alpha carbons of polyketone (Fig. 1) (here we refer this product as PK-allyl anymore). To the best of our knowledge, this is the first time polyketone is modified chemically without changing carbonyl backbone except slightly. Since membrane form of polyketone was used as the starting agent, there will be no need to cast the membrane of the product again. Further functionalizations became possible through double bonds of allyl groups. For example, radicalic polymerization through allyl groups or additions to the allyl double bonds can be used to add extra functionality to the membranes, such as quaternary amines and sulfonic acids which can endow ion-exchanging ability to the membranes. FTIR and NMR measurements confirmed the presence of vinyl groups in the product’s structure.

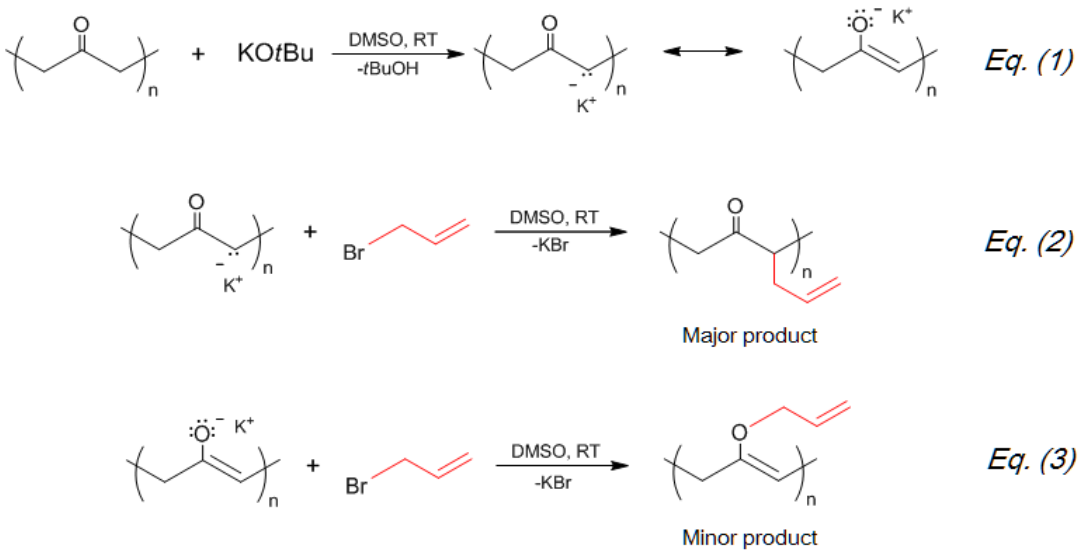

Fig. 1. Reaction scheme for enolization of polyketone and succeeding allylation.

2. Materials and Methods

2.1. Materials

POKETONE was purchased from Hyosung Corp. (Korea). It is the brand name of a polyketone product, which has a molar weight of ~200,000 g/mol. Resorcinol (98.0%) used to make the polyketone membrane was purchased from Samchun. Potassium *tert*-butoxide (98.0%), the strong base used in polyketone synthesis, was purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO, 99.8%) and allyl bromide (99.0%) were purchased from Samchun. All chemicals were used without further purification.

2.2. Synthesis of polyketone membrane

Polyketone, resorcinol and water were charged in a round bottom flask at 10:58.5:31.5 weight ratio. The mixture was stirred and heated at 80 ^{o}C under nitrogen atmosphere for 4 h. The viscous mixture was cast on a glass plate with a doctor blade. The membrane was immersed in toluene, acetone and a mixture of H_2O and methanol respectively in order to wash off resorcinol. Then it was dried in vacuum at 45 ^{o}C. 3 cm x 3 cm pieces were cut for further reactions. Thickness was around 100 μm.

2.3. Synthesis of PK-allyl polymer (membrane)

Cut membranes were charged in a round bottom flask and added 1M KO*t*Bu in dimethyl sulfoxide (DMSO) at

1:1 ratio of ketone and base. As soon as the base was added, color of PK membrane turned dark blue (Fig. 2). This color was maintained until the reaction with allyl bromide. The mixture was stirred slowly under nitrogen atmosphere at room temperature for 24 h. The solution was drawn out of the flask before the next step. 0.5 M solution of allyl bromide (AB) in DMSO was added into the flask at 1:10 ratio of ketone:AB, and waited for another 24 h. When allyl bromide was added, the color of the PK membrane changed to light brown. After washing with DMSO, acetone and ethanol, finally membranes were dried under vacuum at 45 ^{o}C.

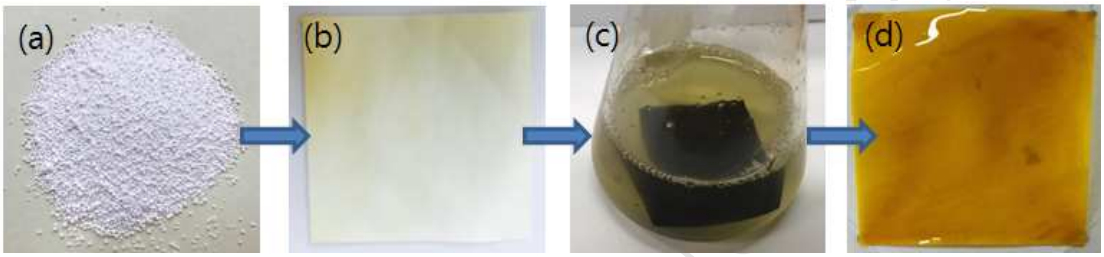

Fig. 2. Images of (a) PK granules, (b) PK membrane, (c) PK membrane when KO*t*Bu was added, and (d) PK-allyl membrane.

2.4. Characterizations

Fourier Transform Infrared (FTIR) spectra were recorded on an IRPrestige-21 equipped with ATR attachment (SHIMADZU Co., Japan). Measurements were conducted at a scan number of 20 and a resolution of 4 cm^{-1} in the range of 4,000 cm^{-1} to 550 cm^{-1}.

FT-Raman spectrum was recorded on a RFS 100/S (Bruker Co., USA) from 100 cm^{-1} to 3500 cm^{-1} at a resolution of 1 cm^{-1}. Nd:YAG laser source emitting 1064 nm excitation lines was used.

UV-Visible spectra were recorded on a UV-Vis Spectrophotometer (S-3100, SCINCO Co., Korea) in the wavelength range from 240 nm to 900 nm at a resolution of 0.95 nm.

^{13}C Solid Nuclear Magnetic Resonance (NMR, Agilent 400MHz 54mm NMR DD2, Agilent Technologies Inc., USA) was used to determine ^{13}C atoms of the solid phase PK-allyl membrane.

Elemental Analysis (EA) was performed to determine whether PK-allyl was synthesized in expected compositional ratio. C, H contents were analyzed on a FlashEA 1112 (Thermo Finnigan, Italia). O content was analyzed on a Flash 2000 series (Thermo Scientific, USA).

X-ray Photoelectron Spectroscopy (XPS, MultiLab 2000, Thermo Fisher Scientific Inc., USA) was used to confirm the chemical composition of the membrane surface of the prepared PK-allyl membrane in the energy analysis range from 0 eV to 2,500 eV.

Scanning Electron Microscopy (SEM, LYRA3 XMU, TESCAN Co., Czech) was used to verify how the morphology of the PK membrane was affected by enolization and final allylation reactions.

The crystal structure of PK membrane and PK-allyl were investigated by a Wide Angle X-ray Diffraction (WAXD) instrument (D8 DISCOVER, Bruker Co., USA) equipped with a 3kW X-ray tube with Cu target source. X-ray reflection patterns were recorded in the range of $5^{o}<2Theta<90^{o}$.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) analyses were carried out on a TGA/DSC 1 (Mettler-Toledo Inc., USA). 5 mg samples were heated from 25 ^{o}C to 800 ^{o}C at a heating rate of 20 ^{o}C/min. Weight changes and energy exchange were observed.

3. Results and Discussion

3.1. Synthesis and general properties

With the attachment of allyl groups, weight of the membranes increased apparently between varying ratios depending on time and other conditions (between 10% - 50%). We carried out all analyses on the samples which showed weight gain around 28%. This means at least ~39% of ketone units were allylated (Degree of allylation≈39%). It should be kept in mind that some polyketone may have somewhat dissolved into DMSO or decomposed during enolization.

A fast color change was observed when KO*t*Bu solution was added. Dark blue color of PK enol may be attributed to a conjugated form of 1,4-diketone enols as depicted in Fig. 3. Actually, broad hydroxide (-OH) peaks observed in FTIR spectra of PK and PK-allyl are also supportive of this insight.

Due to unavoidable self-condensation reactions, PK chains may have cross-linked via double bonds. Supplementary material of this work can be referred to for additional discussion about self-condensation and formation of conjugated groups. Such cross-linking may be the main cause of extensive loss of flexibility. However, shortening of treatment time with KO*t*Bu may help with overcoming this phenomenon and optimization of the mechanical properties. Also, using thinner membranes, varying temperature and choice of solvent can be

considered as imported factors for engineering the flexibility. We used shortened times of enolization and allylation, and lower reagent concentrations, and repeated several cycles of these reactions to improve the flexibility and strength of the membrane. In addition, we tried using THF solvent instead of DMSO. Consequently, we apparently improved the flexibility and mechanical strength of the membranes but more work is required to obtain satisfactory results.

Water uptake test was conducted to compare water uptake capacity and hydrophobicity/hydrophilicity of parent and daughter membranes. PK membranes showed ~120% water uptake and PK-allyl membranes did ~70% water uptake. Attachment of hydrophobic allyl groups seems to have increased the hydrophobicity of PK-membranes.

According to our literature search and our own experiments, PK is not soluble in most common solvents [14]. Hexafluoroisopropanol (HFIP) [35-37], trifluoroethanol [38-42] and *m*-cresol [43-45] are the only known solvents to solve it. Some auxiliary agents can be added to water to prepare aqueous solutions of PK. We used excess amount of resorcinol, which is a bifunctional phenol compound, to assist the dissolution of PK. In our previous work, we used a metal salt mixture for the same purpose. Washing off these agents from membranes leave cavities with large sizes in the membranes. Grafting of PK polymers/membranes with monomers bearing functional group(s) usually decreases the solubility of daughter polymers/membranes. We also confirmed that grafted granules or membranes of PK-allyl are not soluble in all powerful solvents, even if we tried HFIP, trifluoroethanol and *m*-cresol even at elevated temperatures.

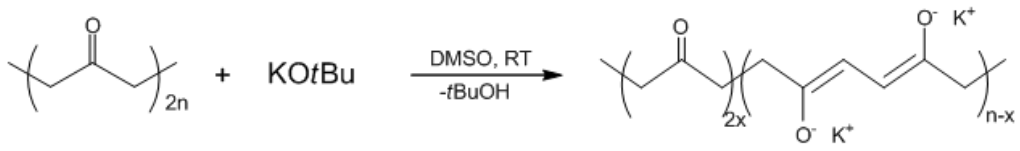

Fig. 3. Schematic representation of enolization of 1,4-diketone unit.

3.2. FTIR Spectroscopy

FTIR spectra of PK membrane and PK-allyl membrane showed clear differences (Fig. 4). FTIR data is good to analyze chemical bonds which exist mainly near surface of the membranes. Two strong peaks were observed at 994 cm^{-1} and 912 cm^{-1} in PK-allyl spectrum, which can be attributed to out of plane bending of pending vinyl groups.

sp^2 (=C-H) stretching was observed around 3077 cm^{-1}. Also, peaks at 1641 cm^{-1}, 1601 cm^{-1} and 1499 cm^{-1} are signs of (C=C) double bond stretchings of vinyl group, enol group and also double bond cross-linking due to self-condesation. Vinyl group and some (C=C) double bonds in the backbone give rise to such modes. These findigns prove the presence of allyl groups in PK-allyl membrane. In addition to these, as carbonyl (C=O) and sp^3 (C-H) stretching modes remained almost unchanged (1690 cm^{-1} and 2912-2953 cm^{-1}), various bending and deformation modes at 1408 cm^{-1}. 1335 cm^{-1}, 1258 cm^{-1}, 1057 cm^{-1}, 809 cm^{-1} became weaker as allyl groups attached to alpha-carbons or oxygens of carbonyl groups through enolate form (Eq. 3 of Fig. 1). 1414 cm^{-1} and 1430 cm^{-1} are sp^3 (-CH_2-) bending peaks of allyl and ketone backbone. 744 cm^{-1} can be attributed to new chain deformation caused by the attachment of allyl groups.

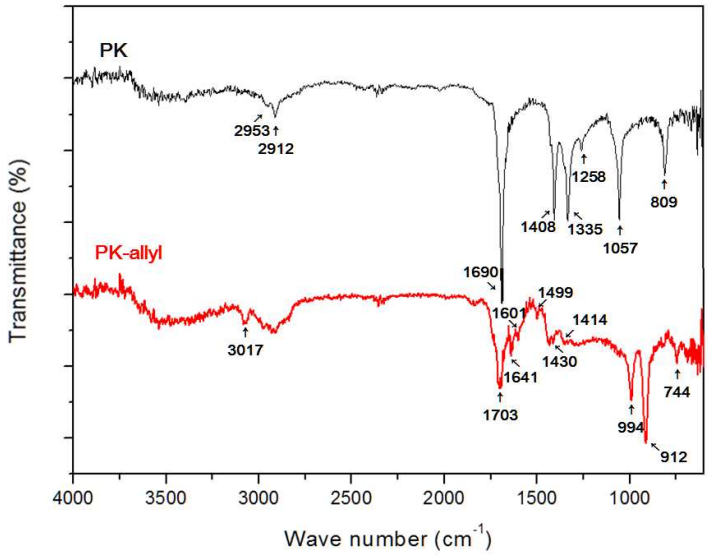

Fig. 4. FTIR spectra of PK and PK-allyl membranes.

In order to check out the effect of enolization reaction on the structure of PK polymer, we neutralized a PK enolate intermediate with acetic acid to see the recovery level back to PK (See supplementary material for the detail). FTIR spectrum showed that almost all peaks are same except for weak C=C peaks around 1550 cm^{-1} and 1650 cm^{-1}, which are probably due to double bonds formed by self-condensation (Fig. S1). Elemental analysis showed that the recovered PK has the following atomic ratios: C: 3.00, H: 3.51, S: <<0.01, O: 0.86. S atom content was beyond detectable limits. This finding shows that there is not a reaction between PK enolate and DMSO

solvent to give permanent products. However, we did not survey if there is such a reaction to from a complex compound of PK and DMSO as an intermediate product. Briefly, there was no detectable Sulfur content in the recovered product of enol or even in the final PK-allyl product. Therefore, we concluded that DMSO doesn't react with intermediate enolate to take place in the structure permanently. On the other hand, it is almost certain that some condensation reactions occur although its extent is much smaller than that occurs in a homogeneous environment.

Further functionalization of PK-allyl polymer membrane is possible through addition and radicalization reactions on allyl double bonds. Although such work is being carried out by our group to obtain ion exchange membranes derived from PK for the sake of desalination applications, complete and thorough results including ion exchange application tests are considered as another publication. Even so, we carried out a demonstrative work to observe the function of double bonds in PK-allyl in a typical functionalization reaction and succeeding modifications. A sulfonation reaction as described in supplementary material was carried out on PK-allyl membrane. FTIR data showed that two O=S=O peaks appear around 1000 cm^{-1} and 1200 cm^{-1}, and two characteristic allyl peaks (vinyl peaks) at 994 cm^{-1} and 912 cm^{-1} almost disappears (Fig. S4). Presence of C=C peaks around 1550 cm^{-1} and 1650 cm^{-1} is probably due to enols, double bond formation due to further self-condensation and dehydration in strong acidic media. Discoloration trend of membranes can be seen in the photos shown in Fig. S5. Elemental analysis results also showed that there are sulfur atoms in the structure (Found formula: $C_3H_{3.23}S_{0.16}O_{1.07}$). According to these results, sulfonation of double bonds in PK-allyl yield sulfonic acid and/or sultone groups. Possible reaction and structure of products are shown in Fig. S6.

3.3. FT-Raman Spectroscopy

Raman spectroscopy of PK membrane, which aids to identify surface characteristics of the membranes, showed two peaks at 2900-3000 cm^{-1} region for C-H bonds, a peak at 1708 cm^{-1} for C=O group, peaks for methylene groups ($-CH_2-$) at 1441, 1416, 1357 and 1252 cm^{-1} and a peak for C-C bond at 1102 cm^{-1} (Fig. 5) as observed in FTIR spectrum (Fig. 4).

Raman spectroscopy results also proved the presence of (=C-H) bonds of pending allyl groups with peaks at

3003 cm^{-1} and 3081 cm^{-1}, which could be better seen herein than in FTIR. A strong peak due to (C=C) bond was observed at 1640 cm^{-1}, and also 1638 cm^{-1} shoulder and 1510 cm^{-1} peaks denote such (C=C) double bonds in allyl groups and tentative enol groups. (C=O) bond peak appeared at 1700 cm^{-1} as a weaker bond in Raman. 923 cm^{-1} and 1000 cm^{-1} peaks also indicate (=CH_2) of allyl group.

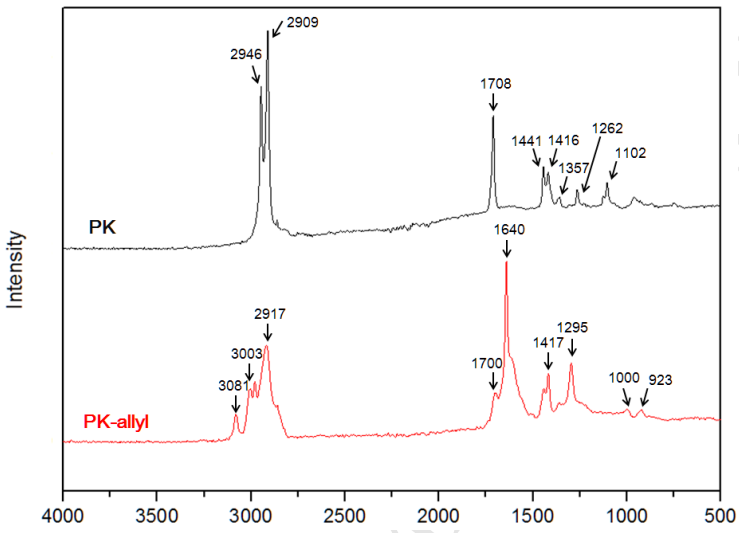

Fig. 5. Raman spectra of PK and PK-allyl membranes.

3.4. UV-Visible Spectroscopy

PK membrane surface showed two absorbance peaks at 277 nm (λ_{max}) and 361 nm (Fig. 6). 277 nm is due to the absorption by electronic transition of non-bonding electrons of carbonyl group (C=O) to π antibonding orbital (n→π*). Weaker absorption at 361 nm can be attributed to electronic transitions in conjugated enols whose structure is similar to that shown in Fig. 3. Such conjugated structures require lower energy as in the case of 2,4-pentanedione. PK-allyl membrane showed two peaks at 260 nm and 318 nm (λ_{max}). Energy required for n→π* became a little lower whereas λ_{max} value moved to a longer wavelength which means that number of conjugation incidents and probably their length increased due to self-condensation reactions. Addition of allyl group on the oxygen of an enolate may foster conjugations. Absorbance grew in all wavelengths, due to addition of double bonds of allyl groups to the system. Even at up to 700 nm, there is slight absorbance which is the main reason for red-brown color of the PK-allyl membranes. Further discussion about self-condensation and subsequent conjugations can be found in Supplementary Material. It should be noted that these data mostly refers to the surface

characteristics of all membranes.

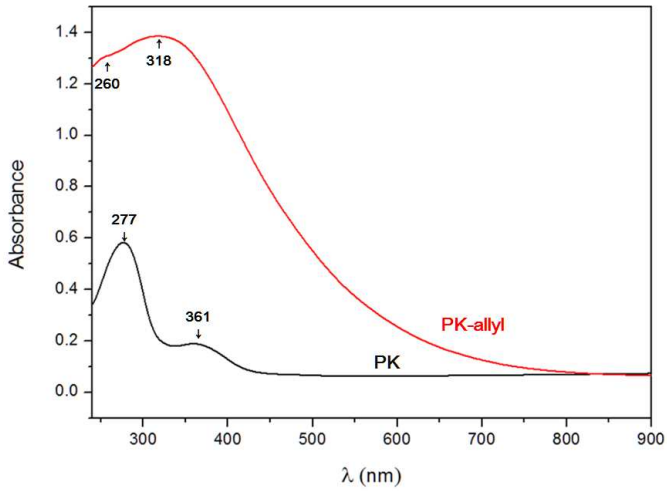

Fig. 6. UV-Vis spectra of PK and PK-allyl membranes.

3.5. ^{13}C Solid NMR Spectroscopy

A broad peak at 40.6 ppm denotes sp^3 carbons of PK chain and allyl groups (Fig. 7). At 121.8 ppm & 139.2 ppm, two sp^2 carbons of vinyl groups were observed. At 213.6 ppm, carbonyl group shows a peak. Nearby this, spectrum also shows weak carbonyl peak at 178.7 ppm, which probably implies the presence of enol form binding an allyl group onto the oxygen. A peak at 74.3 ppm also signals the binding of sp^3 carbon ($-CH_2-$) of allyl group to the oxygen of carbonyl group. Nonetheless, the latter two peaks show weak intensity and may not be regarded as significantly precise assignments as the abundances of C2' and C4' carbons are not expected to be high.

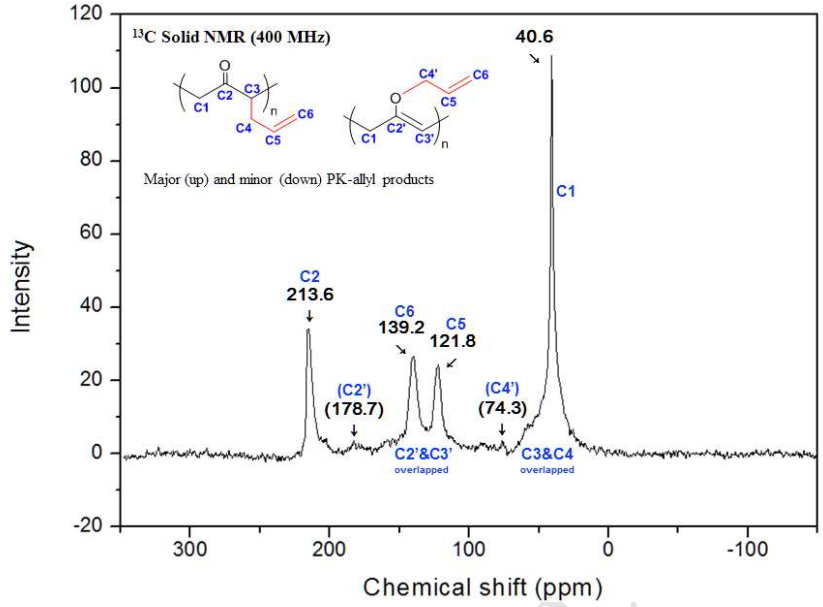

Fig. 7. ^{13}C NMR spectrum of PK-allyl membrane. Since C2' and C4' peaks have weak intensity, these two should not be regarded as significant assignments.

3.6. Elemental Analysis

Theoretically calculated formula for PK-allyl in case of 100% allylation yield is C_6H_8O (1:1 carbonyl:allyl). It means a 71.4% weight increase can be expected if 100% allylation occurs. For the analyzed PK-allyl product, allylation yield and weight increase were found ~39% and ~28%, respectively. Found formula has been $C_{6.12}H_{7.38}O$ or $C_{6.00}H_{7.23}O_{0.98}$, which denotes the occurrence of some dehydration due to self-condensation. Although oxygen ratio is measured separately and may not be credible, C/H ratio provides some evidence about structural conversions so as to judge about dehydration. Increased C/H ratio is an evidence for the supposed dehydration reactions (self-condensation). Dehydration phenomenon explains why C/O ratio is not lower than 6 as expected for lower allylation yields.

Lower allylation ratios may help preserve the mechanical properties of PK to a greater extent. Also, for many applications such as ion-exchange technology, less number of functional groups may meet the required levels of ion-exchange capacity. Therefore, degree of allylation can be kept lower for preserving the structure and mechanical strength of PK polymer better. We worked on products of high allylation yield this time to prove the concept.

3.7. X-Ray Photoelectron Spectroscopy (XPS)

Fig. 8 shows the XPS analysis result of PK-allyl membrane surface. In this experiment, the C/O ratio was found to be 6.09, which is very close to the theoretical C/O ratio of 6. This ratio is in accordance with that found by elemental analysis. The majority of elemental count belongs to C and O atoms. There was negligible amount of Br atom as can be seen on the low energy side of the graph. Therefore, it was concluded that the allyl groups were well attached to the backbone of polyketone, and also washing steps were sufficient for the removal of KBr.

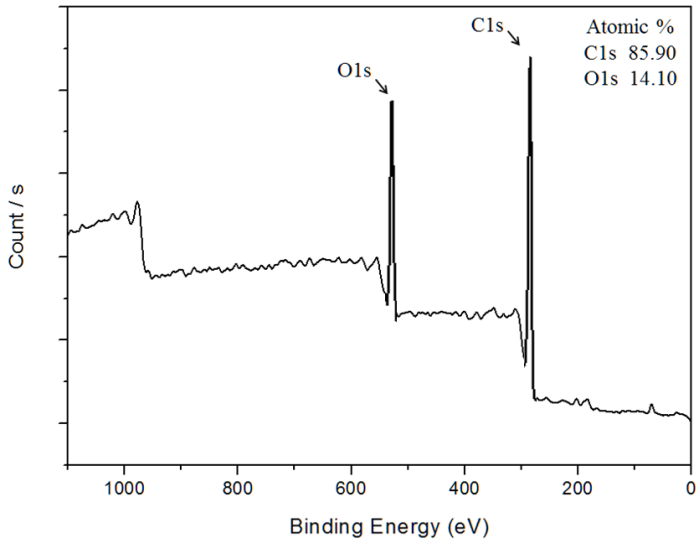

Fig. 8. XPS spectrum of PK-allyl membrane.

3.8. Scanning Electron Microscopy (SEM)

Surface morphology of PK was mostly preserved. No major cracks or large holes formed on the surface of PK-allyl. The cross-section images show that (Fig. 9b), due to the extensive use of resorcinol as auxiliary solving agent for PK, large pores formed within the membrane. This mesoporous structure was not affected too much by all reaction process as cross-section images of PK-allyl imply. Large cavities up to 3-8 μm size can be observed in cross-section images however, walls of these cavities are almost intact.

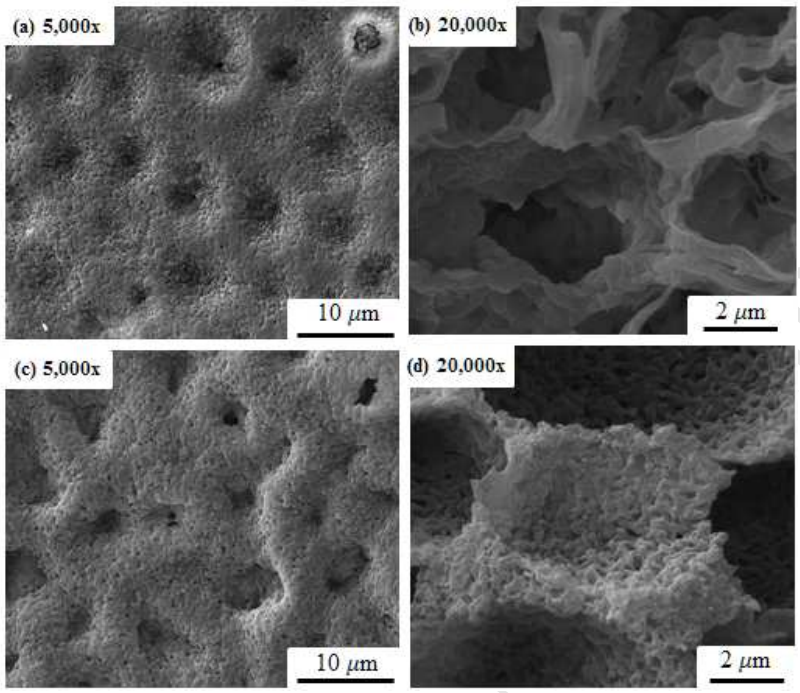

Fig. 9. SEM images of PK and PK-allyl membranes: (a) PK surface; (b) PK cross-section; (c) PK-allyl surface; (d) PK-allyl cross-section.

As to the difference in the looks of the morphologies seen on cross-sections images, porosity extent and wall texture seem to have changed slightly due to enolization and allylation reactions. Even though polyketone and intermediate enol are not considerably soluble in DMSO, the solvent is absorbed by the polymer, and thus physical structure can be modified by the process which may be resulting in realignment of pores and wall texture as it happens in thermal process of plastics and other solid materials.

3.9. Wide Angle X-ray Diffraction (WAXD)

Ohsawa et al. [7] and many others demonstrated X-ray diffraction patterns for PK polymers. Although cast with a different method herein, PK membranes showed patterns of α-form as was in their work. PK membrane showed typical crystalline peaks, at $2\theta=17.4^{o}$, 21.7^{o}, 24.6^{o}, 26^{o}, 31.5^{o}, 37.9^{o}, 39.5^{o} and 41.8^{o}. These correspond to (101), (110), (111), (200), (210), (103), (212) and (301) reflections at room temperature. Attachment of allyl groups to PK

backbone did not alter the main 2θ angles for (110), (200), (210) and (301) reflections much in the case of PK-allyl. However, a new reflection was observed at 2θ=11.5°, which may possibly denote a new reflection caused by staked allyl groups. These results would be anticipated since the polymer did not change from solid state to another neither it underwent a severe thermal process.

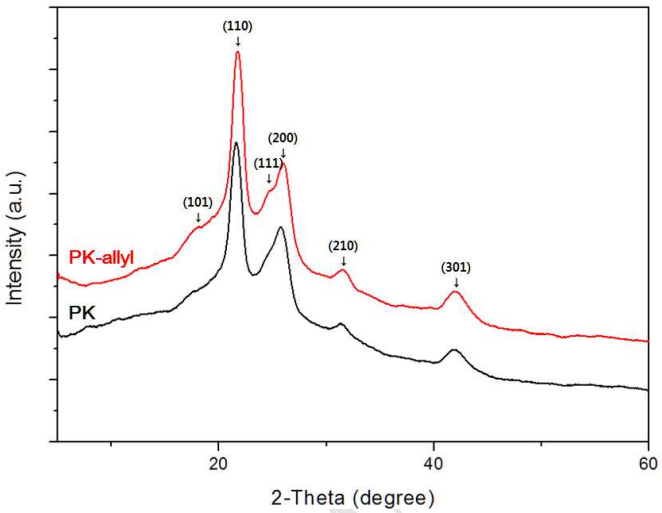

Fig. 10. Wide angle X-ray diffraction (WAXD) patterns of (a) PK membrane and (b) PK-allyl membrane.

3.10. Thermal Analysis

Thermogravimetric analysis (TGA) data show that weight loss starts earlier for PK-allyl than for PK around 130 °C (Fig. 11). This may be attributed to allyl groups bound to oxygen of carbonyl group in enol form. Relative stability of allyl radical and cation intermediates can drive a decomposition mechanism which suggests the cleavage of allyl from PK backbone.

Decomposition rate of PK-allyl increases sharply after 390 °C with a final weight loss of 76.0%. PK membrane preserves its weight to a greater extent until 242 °C, though. A more stepwise weight loss process occurs in the case of PK. First major weight loss happens around 294 °C by 23.8%. In the second stage, another weight loss occur around 460 °C by 36.2%. The total weight loss for PK was observed around 60.0%. The difference between weights of two residues can be explained with pending allyl groups of PK-allyl.

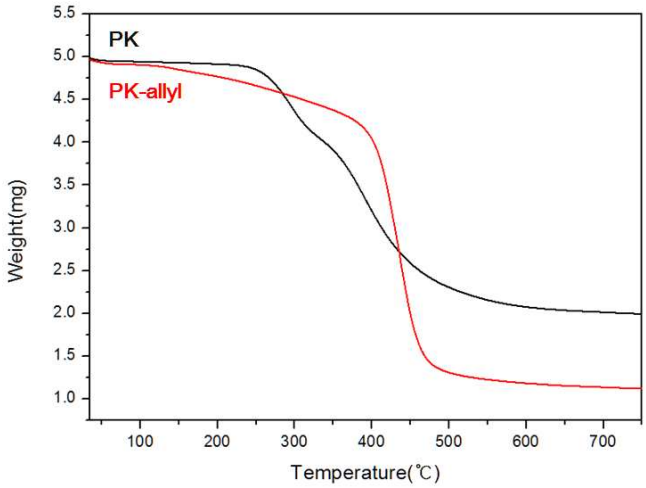

Fig. 11. TGA curves of PK and PK-allyl membranes.

4. Conclusions

Functional modification and monomer grafting of polyketone polymer was successfully carried out by simple chemical methods despite the fact that polyketone is among the most chemically resistant thermoplastic polymers. We succeeded to attach unsaturated substituents to the polyketone backbone with allylation process on polyketone enolates. We obtained the PK-allyl product physically in membrane form, since PK reacts in solid state and as a membrane with all solutions of chemicals used in our experiments. Thus, there is no need to cast a membrane of PK-allyl by dissolving it in a solvent since it is insoluble in common solvents. SEM images slightly give the idea that allylation occurs almost evenly throughout the whole depth of the membrane. We believe that, through these pending allyl groups, miscellaneous functional groups can be further attached to PK-allyl via addition reactions to the doubles and Atom Transfer Radical Addition reactions in the presence of radical initiators. Alternative polymerization can be started with ionic initiators so that ionic polymerization can occur between allylic double bond and grafting agents.

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Conflicts of interest: none.

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Highlights

- **First** chemical grafting method for heavy-molecular-weight polyketone (PK) polymers.
- **Carbonyl** groups not interfered and only **aliphatic** part is mainly used for substitution.
- **Heteregenous reaction** allowed a **membrane of allylated polyketone** (PK-allyl).
- **Further functionalization** of PK-allyl polymer is possible via addition and polymerization.
- **Flexibility** weakens, but membranes preserve **thermal** and apparent **mechanical strength**.

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