

# Characterization of Methyl-Substituted Polyamides Used for Reverse Osmosis Membranes by Positron Annihilation Lifetime Spectroscopy and MD Simulation

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**ABSTRACT:** Three kinds of polyamides were synthesized from three diamines and 1,3,5-benzenetricarbonyl trichloride (TMC). The diamines used were *m*-phenylene diamine, *N*-methyl-*m*-phenylenediamine, and *N,N'*-dimethyl-*m*-phenylenediamine. The average free volume sizes of the polyamides were measured by positron annihilation lifetime spectroscopy (PALS), and the free volume fractions were evaluated by molecular dynamics (MD) simulations. The methyl substitution on amino groups of diamines brought about an increase in interstitial space of molecular chains of the polyamides. In addition, reverse osmosis (RO) membranes were prepared by interfacial polymerization from the three diamines and TMC. The

increase in the degree of methyl-substitution of diamines led to increased chlorine resistance and decreased salt rejections of the polyamide RO membranes. Thus, the methyl-substitution of diamines significantly influenced membrane performance. The vacancy sizes and fractional volumes in polyamides evaluated by PALS measurement and MD simulation were well correlated with salt rejection of polyamide RO membranes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1757–1762, 2009

**Key words:** reverse osmosis membrane; positron annihilation lifetime spectroscopy; molecular dynamics simulation; chlorine resistance; free volume

## INTRODUCTION

For reverse osmosis (RO) treatment, thin film composite (TFC) membranes with high flux have been widely developed.<sup>1</sup> Aromatic polyamides are mainly used in the thin film polymers of TFC membranes in commercial use. The control and clarification of the polyamide structures is essential to improve membrane performance.

In our previous works, the size of the interstitial space among the molecular chains, called vacancy, was one of the key factors in controlling salt rejections of typical RO membranes.<sup>2,3</sup> Positron annihilation lifetime spectroscopy (PALS) with a variable energy positron beam was applied to detect such vacancies that are related to RO performance of the polyamide-based thin film composite membranes. When positrons are implanted in polymers, they often form positronium (Ps), consisting of the incident positron and an electron from the substrate in a bound state. Ortho positronium (*o*-Ps) overlaps with peripheral electrons in local vacancy with sizes on a

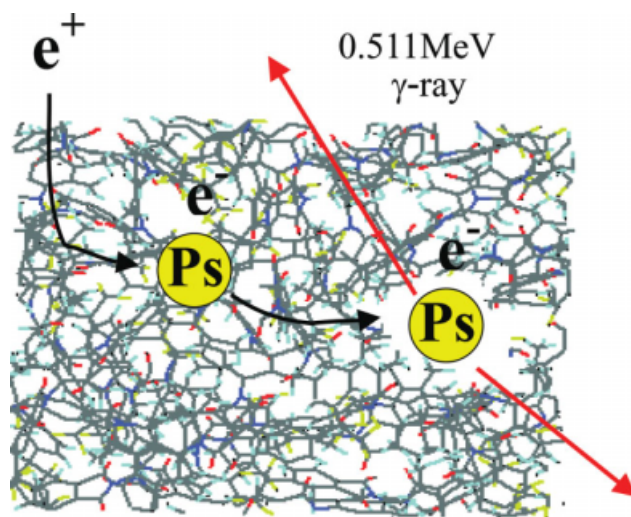
scale of angstroms to nanometers, undergoes pick-off annihilation, and emits gamma rays. The lifetime of *o*-Ps and its energy carry information about vacancy profile. Figure 1 presents a schematic diagram of PALS technique.

Kwak and coworkers<sup>4</sup> applied the PALS technique to explain the flux-enhancement mechanism in TFC membranes prepared using DMSO as an additive. The PALS results showed increase in pore size by the addition of DMSO. The correlations between RO performances and *o*-Ps lifetime parameters were clearly described.

An interesting approach to the characterization of vacancy profiles in polymers is the use of molecular simulations. We previously found that molecular dynamics (MD) simulation was useful for characterizing the vacancy profiles of some amorphous polymers.<sup>3,5</sup>

The aim of this study was to clarify the influence of methyl substitution on amino groups of diamines on vacancy profiles and corresponding RO performances of typical polyamide-based thin film composite membranes. Therefore, three kinds of diamines with different methyl substitution degrees were used for the preparation of polyamides. The relationship between the vacancy profile and the RO performance was discussed based on PALS and MD data.

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**Figure 1** Concept of local vacancies probed by Ps in polymer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

## EXPERIMENTAL

### Materials

Analytical grade *m*-phenylene diamine (MPD) was purchased from Wako Pure Chemical Industries (Osaka, Japan), and analytical grade 1,3,5-benzenetricarbonyl trichloride (TMC) was purchased from Tokyo Kasei Kogyo (Tokyo, Japan). *N,N'*-dimethyl-*m*-phenylenediamine (*N,N'*-DMMPD) was synthesized according to the patent.<sup>6</sup> *N*-methyl-*m*-phenylenediamine (*N*-MMPD) was also synthesized according to the patent.<sup>7</sup> The purities of the synthesized *N,N'*-DMMPD and *N*-MMPD were more than 99%. Polysulfone (PSf), used for the preparation of a porous support substrate, was purchased from Solvay Advanced Polymers (Udel P-3500).

### Polymer preparation

A 100 mL aqueous MPD (22.6 mmol) solution with NaOH (45.0 mmol) was slowly dropped into a 100 mL TMC (15.1 mmol) hexane solution. In the cases of *N*-MMPD and *N,N'*-DMMPD, diamine solutions were 40 wt % 2-propanol aqueous solutions with NaOH (45.0 mmol). The moles of *N*-MMPD and *N,N'*-DMMPD were 22.6 mmol in the 100 mL solutions. The TMC solution and the polymerization procedure were the same as that used for MPD. The three kinds of precipitated polymers were filtered, washed with acetone, and dried at 80°C for a day.

Fourier transform infrared spectroscopy (FTIR) analyses (JASCO FT/IR-470) for the three obtained polyamides were carried out to confirm polymerization.

### Positron annihilation lifetime spectroscopy

The positron source, about 0.4-MBq <sup>22</sup>Na sealed in thin kapton foil, was sandwiched between two identical polyamide sample film stacks with a thickness of ~ 1 mm. The sample was placed in a vacuum cell. A conventional fast coincidence system with a time resolution of 260 ps at the full width at half-maximum was used to measure the positron annihilation lifetime spectroscopy (PALS) at room temperature. Each spectrum was analyzed with the MELT<sup>8</sup> program. One million counts were taken for every sample. The time resolution of PALS was 0.26–0.30 ns. The detail procedure for the PALS measurements is described in a previous article.<sup>2</sup>

### Molecular simulation

Molecular modeling of the polyamides was carried out with the molecular dynamics (MD) program of MS modeling 4.0 (Accelrys). The steric structures and electrostatic charges of the repeat units of polyamides were determined by geometry optimization calculations based on density functional theory (DFT) using the B3LYP algorithm.<sup>9</sup> Amorphous polyamide models were constructed by connecting each repeat unit model up to 30–40. Constant number, pressure, temperature (NPT)<sup>10</sup> and constant number, volume, temperature (NVT)<sup>11</sup> methods were used for the MD calculations to obtain stable structures of the polyamide packing models having real densities at 298 K. The details of the modeling procedure are described in the literature.<sup>8</sup>

### Membrane preparation

Microporous support substrate was first prepared to obtain the thin film composite (TFC) membranes. A solution of 18 wt % polysulfone (PSf) in *N,N*-dimethyl formamide was cast on a glass plate using an applicator with 254 μm gap. The glass plate was immediately immersed in a water bath at room temperature to obtain the porous membrane. The porous PSf membrane was rinsed with water and stored in deionized water.

For the preparation of the polyamide membrane from *N,N'*-DMMPD and TMC, the support PSf membrane was immersed in an aqueous solution of *N,N'*-DMMPD (3 wt %), sodium lauryl sulfate (0.15 wt %), triethylamine (2.5 wt %), camphorsulfonic acid (5 wt %), and 2-propanol (40 wt %) for 30 s and pulled up slowly. Excess diamine solution was removed from the surface of the PSf support membrane. The PSf substrate was then covered with a solution of 0.2 wt % TMC in a hydrocarbon solvent (isoparaffin, Idemitsu Petroleum, IP-1620) for 10 s to deposit the polymeric thin layer on the substrate by

interfacial reaction. The resulting TFC membrane was dried at 140°C for 2 min.

A similar method was used for the preparation of the polyamide membrane from *N*-MMPD and TMC. The aqueous solution used for the interfacial reaction was a solution of *N*-MMPD (2.0 wt %), sodium lauryl sulfate (0.15 wt %), triethylamine (2.0 wt %), and camphorsulfonic acid (4.0 wt %). The organic solution was a hydrocarbon solvent (isoparaffin, Idemitsu Petroleum, IP-1016) containing TMC (0.3 wt %). The PSf support was first immersed in the aqueous *N*-MMPD solution and then covered with the organic TMC solution for 60 s to deposit the polymeric thin layer on the substrate by interfacial reaction. The membrane was dried at 120°C for 3 min. The membrane preparation condition for *N*-MMPD was different from that for *N,N'*-DMMPD. This is because the preparation condition was optimized to obtain a high salt rejection.

For the polyamide membrane prepared from MPD and TMC, a commercial membrane (Nitto Denko, NTR-759HR) was used.

### Membrane performance

Salt rejection and water permeability were measured for a 1500 ppm NaCl solution with pH = 6.5–7 at

25°C using the common continuous pump-type RO apparatus under the applied pressure of 1.5 MPa.

For the measurement of chlorine resistance, the membrane was immersed in aqueous sodium hypochlorite solution (200 ppm) with calcium chloride (500 ppm) as an oxidation accelerator<sup>12</sup> at pH = 7.0 at 40°C for 48 h. The membrane performance was checked every 12 h.

## RESULTS AND DISCUSSION

### Characterization of polyamides and RO membrane performance

Figure 2 shows three reaction schemes for the polymerized polyamides. Hereafter, the polyamides synthesized from MPD, *N*-MMPD, and *N,N'*-DMMPD are abbreviated as M0, M1, and M2, respectively.

Figure 3 shows FTIR results for three polyamides. The peaks at 1645–1660 cm<sup>-1</sup> that appeared in all polyamides are attributed to C=O stretching of amide group. The peaks at 1490 cm<sup>-1</sup> and at 1590–1610 cm<sup>-1</sup> were also observed in all polyamides, which are attributed to C–C stretching of benzene ring. On the other hand, the peaks at 1540 cm<sup>-1</sup> attributed to N–H deformation of amide group were observed only for M0 and M1 samples. This is because no N–H bond existed in the M2 sample. The samples

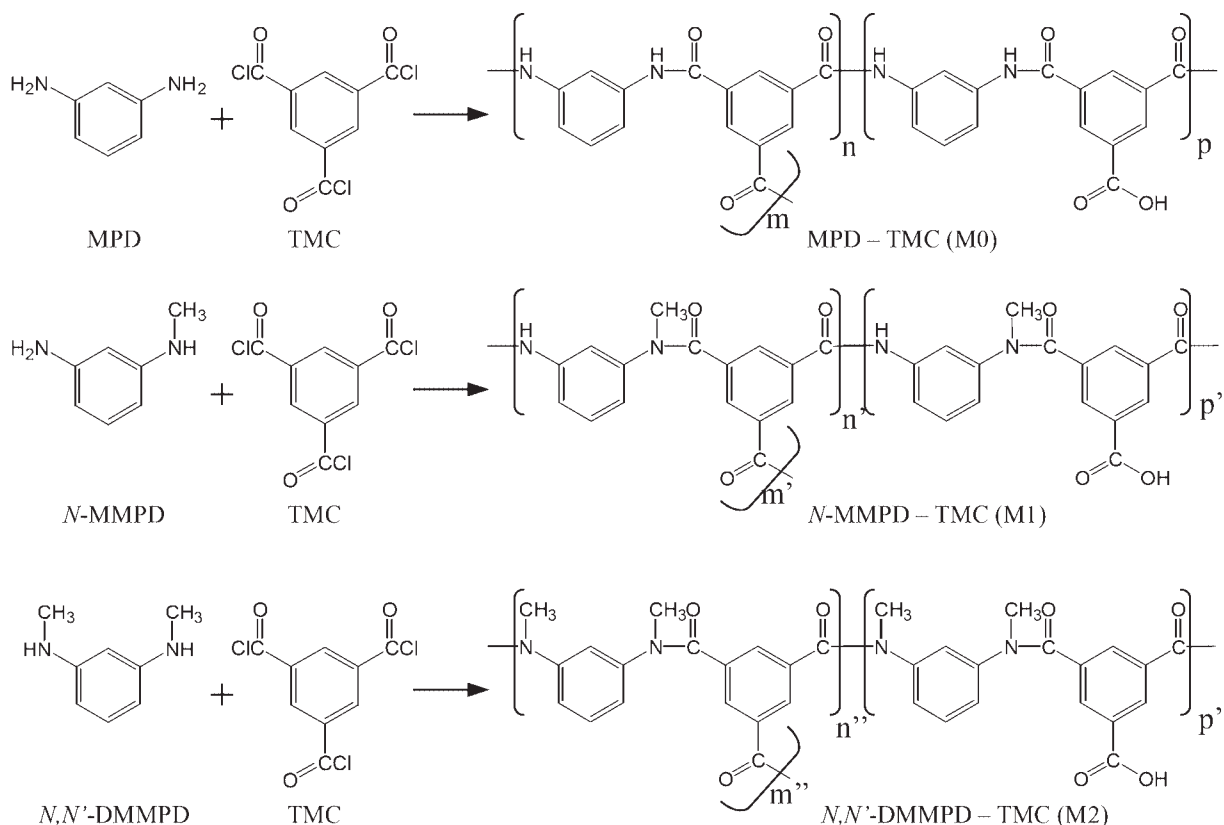
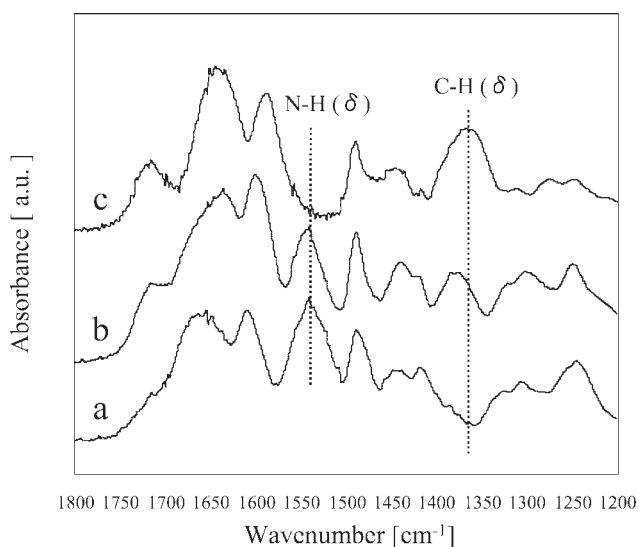


Figure 2 Schemes of polymerizations.



**Figure 3** FTIR spectra of (a) M0, MPD-TMC; (b) M1, *N*-MMPD-TMC; (c) M2, *N,N'*-DMMPD-TMC.

M1 and M2 showed the peaks at  $1370\text{ cm}^{-1}$ , which is attributed to C—H deformation of the  $\text{CH}_3$  group bonded to amide group. This is reasonable because the M0 sample had no methyl-substitution on amino groups.

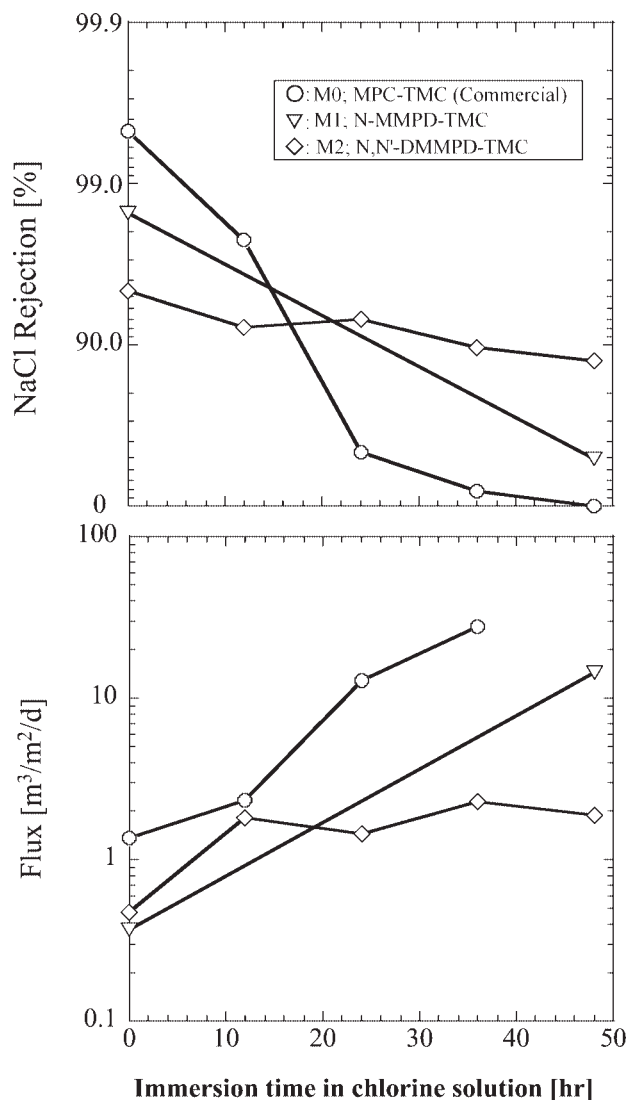
The RO performances of three polyamide membranes are summarized in Table I. The salt rejection increased in the following membrane order: M2, M1, and M0. This means that the decrease of methyl-substitution on amino groups brought about the higher salt rejection. The M0 membrane showed the highest flux. Flux is related to thin layer thickness. Although the thin layer thickness of the M0 membrane may be small, further investigation is necessary for confirmation.

Figure 4 shows the effect of immersion time in the chlorine solution on membrane rejection and membrane flux. Membrane performances were compared for the three membranes. Initially, NaCl rejection increased in the membrane order M2, M1, and M0. However, this order was reversed after immersion in the chlorine solution for 48 h. This means that the membrane prepared from *N,N'*-DMMPD and TMC (M2) showed the lowest reduction of NaCl rejection and the highest chlorine resistance. The chlorine resistance increased in the membrane order M0, M1, and M2. As discussed in our previous article,<sup>13</sup> the reactive site of active chlorine was suggested to be

**TABLE I**

**Membrane Performances for Three Kinds of Membranes**

| RO membranes               | Rej. (%) | Flux ( $\text{m}^3/\text{m}^2/\text{d}$ ) |
|----------------------------|----------|---|
| M0, MPD-TMC                | 99.5     | 1.36                                      |
| M1, <i>N</i> -MMPD-TMC     | 98.5     | 0.37                                      |
| M2, <i>N,N'</i> -DMMPD-TMC | 95.3     | 0.47                                      |



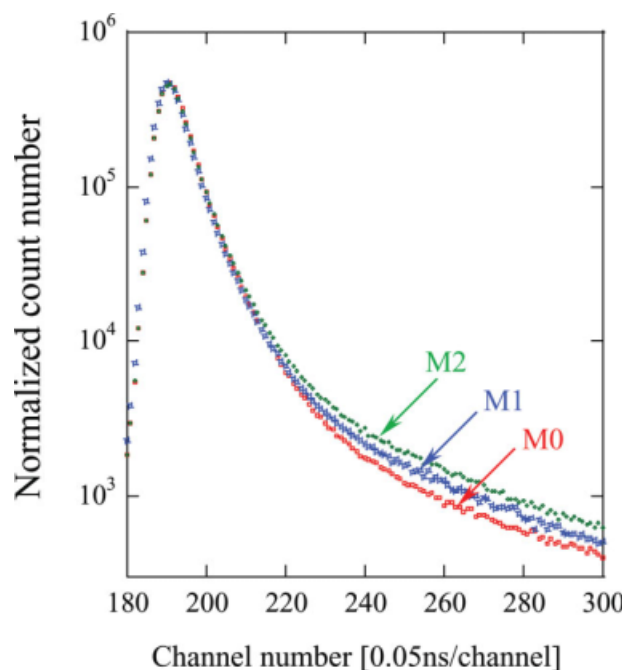
**Figure 4** Effect of immersion time in chlorine solution on membrane rejection and membrane flux.

the N—H part in the amide bond. Thus, decrease in the number of N—H bonds in the diamines used for the polymerization by the methyl substitution brought about higher chlorine resistance.

### PALS measurement

Positron annihilation was used to assess the free-volume void sizes in three kinds of polyamides with different degrees of methyl substitution (M0 = no methyl substitution; M1 = one methyl substitution; M2 = two methyl substitution). Figure 5 shows the positron annihilation lifetime spectra in three kinds of polyamides. The higher that the degree of methyl substitution is at the amide bond of the polyamide, the slower the positron lifetime spectral decay. This indicates that the subnanometer voids in the free volume of the polyamides become larger with a higher degree of methyl substitution.





**Figure 5** Positron annihilation lifetime spectra in three kinds of polyamides. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

According to a simple model, vacancy is approximated by an infinite height potential well, and the electrons available for the pickoff annihilation are assumed to exist as an electron layer on the surface of the well with a thickness  $\Delta R$ . The *o*-Ps lifetime  $\tau_3$  is then related to the vacancy radius  $R$  as follows<sup>3,14</sup>:

$$\tau_3 = 0.5[1 - R/(R + \Delta R) + \sin(2\pi R/(R + \Delta R))]/2\pi]^{-1} \quad (1)$$

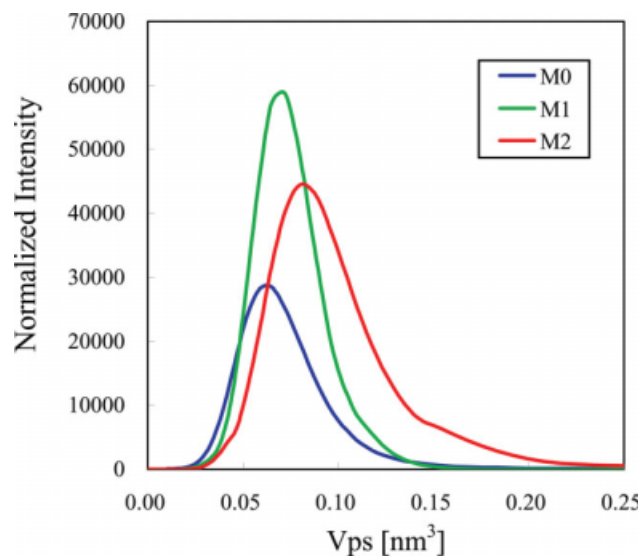
where  $\Delta R = 0.166$  nm is known to have excellent agreement with the experimental data.<sup>15</sup>

The average radius  $R$  of vacancies was estimated from the spectra in Figure 5 and eq. (1). Average radii were in the range of 0.2–0.4 nm. If it is assumed that the free-volume voids are spherical, the average size of vacancy  $V_{Ps}$  can be estimated by  $4\pi R^3/3$ .

Figure 6 shows  $V_{Ps}$  curves for three polyamides. The  $V_{Ps}$  values at peak positions in Figure 6 are summarized in Table II.  $V_{Ps}$  tends to increase with the degree of methyl substitution of the diamine. The methyl substitution of diamine makes the diamine more bulky, resulting in a larger  $V_{Ps}$ .

### MD simulation

MD simulation of the three polyamides was performed by using the procedure employed in our previous study.<sup>3</sup> Figure 7 shows the packing structure obtained by the MD simulation of polyamides



**Figure 6** Vacancy size probed by PALS for three kinds of polyamides. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

with no methyl substituent, one methyl substituent, and two methyl substituents. The red and blue regions in Figure 7 correspond to the polymer chain and the free volume, respectively. The difference in the ratios of the blue region's volume to the red region's volume is not clear for these three cases. Therefore, the following quantitative analysis was carried out. The fractional free volume (FFV) is given by eq. (2).<sup>16</sup>

$$\text{FFV} = \frac{V_{298} - V_0}{V_{298}} \quad (2)$$

where  $V_{298}$  is the cell volume obtained through simulation.  $V_0$  can be obtained with eq. (3) by using van der Waals volume,  $V_w$ .<sup>17</sup>

$$V_0 = 1.3 V_w \quad (3)$$

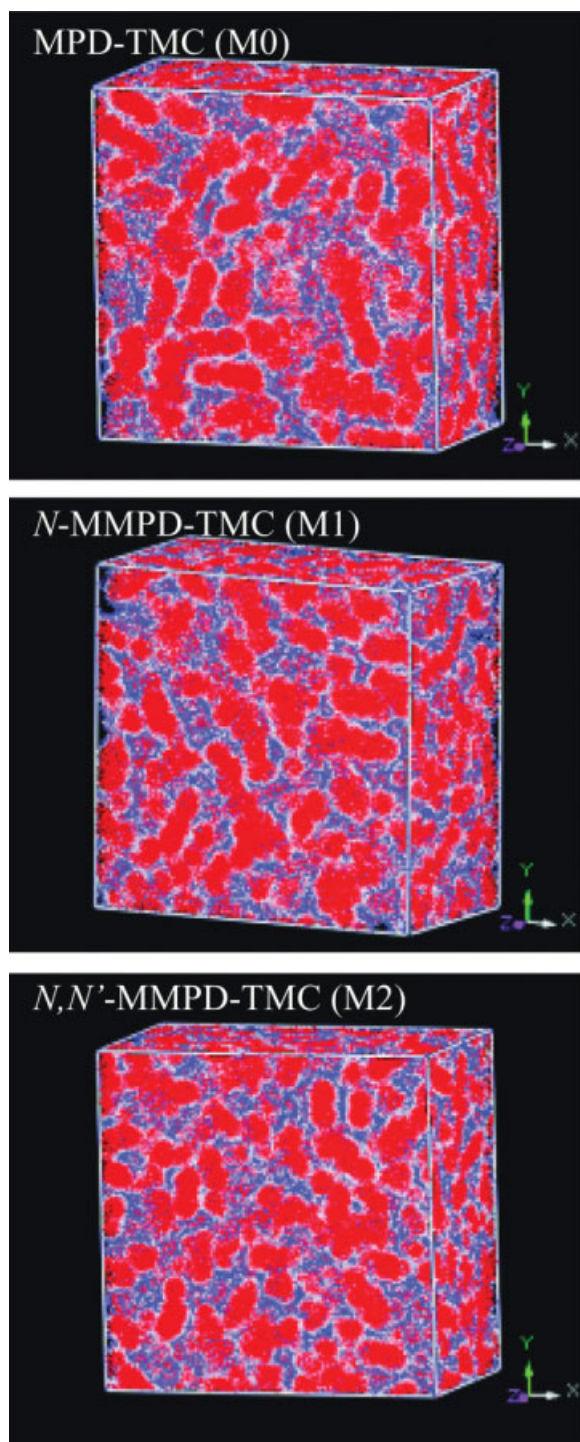
$V_w$  was estimated by using MS Modeling 4.0 software (Accelrys) based on molecular dynamics simulation results shown in Figure 7.

The obtained FFV data are summarized in Table II. This MD simulation also indicated that an increase in methyl substitution resulted in an increase in molecular packing efficiency and free

**TABLE II**  
Vacancy Size and Fractional Free Volume in Polyamides

| Diamine    | $V_{Ps}$ (nm <sup>3</sup> ) | FFV <sub>MD</sub> (–) |
|------------|-----------------------------|-----------------------|
| MPD        | 0.062                       | 0.119                 |
| N-MMPD     | 0.071                       | 0.134                 |
| N,N'-DMMPD | 0.081                       | 0.142                 |

$V_{Ps}$ , average vacancy volume size by PALS; FFV<sub>MD</sub>, fractional free volume simulated by MD calculations.



**Figure 7** Molecular dynamics simulation results of three kinds of polyamides. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

volume fraction. Besides the average vacancy size,  $V_{Ps}$ , obtained by positron annihilation, the FFV increased by methyl substitution. This means that not only the increase of free volume size but also the increase of free volume fraction can be attributed to

methyl substitution. By the comparison of  $V_{Ps}$  and FFV data with NaCl rejection shown in Table I, it was found that the NaCl rejection is closely correlated with the  $V_{Ps}$  and FFV values. In other words, we recognized the tendency that NaCl rejection increases as the free volume in the membrane decreases.

## CONCLUSIONS

Vacancy profiles in three kinds of polyamides were measured by the PALS method. The average free volume size increased as the numbers of methyl substitution on amino groups of diamines increased. It was found by MD simulation that methyl substitution also brought about an increase of the free volume fraction. The RO membranes with these three kinds of polyamides were prepared by interfacial polymerization. As methyl-substitution on amino groups increased, chlorine resistance became higher and NaCl rejection decreased. The salt rejection was well correlated to both the free volume size measured by the PALS measurement and the free volume fraction evaluated by the MD simulation. This indicates that PALS measurement and MD simulation are useful ways to predict the salt rejection property of RO membranes.

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