# Correlation between Roughness of Nanowires and Polymer Backbone Conformation

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## Introduction

As the minimum dimensions of integrated circuits decrease, the resolutions used in lithography approach the dimension of molecular size. The reduction of line-edge roughness (LER) and line-width roughness (LWR) in resist patterns is the most important issue in the area of lithographic techniques and directly affects critical dimension (CD) control in sub-100 nm patterning. The material origins of LER have been investigated vigorously, but the information is still incomplete. The effects of the lithographic process,[1,2] reactions of polymer molecules in the base resin,[3] and acid diffusion processes,[4,5] among others, have been shown to correlate with LER; however, these factors are intricately intertwined to give the overall LER in the resist pattern. The conformation of the polymer chain in the base resin, along with molecular weight and polymer distribution, are the most crucial primary factors in determining roughness. This has been demonstrated not only by experimental analysis[6] but also via simulations based on the statistical theory of polymer backbone conformation.[7]

We recently reported the formation of nanostructures by single particle negative-tone imaging (SPNI).[8−11] High-energy charged particles were used to fabricate 1-D nanowires along their trajectories as they penetrated into polymer films, and a nonhomogeneous cross-linking reaction induced in the nanometer-scale cylindrical area resulted in a linear nanogel (nanowire) whose length was controlled by the range of the incident particle.[8,9] The thickness of the nanowire has been revealed to be a function not only of the energy density deposited by the incident particle[10] but also of the molecular weight and backbone conformation (molecular shape) of the target polymer.[11,12] Additives such as cross-linkers and acid generators are not required in the SPNI technique; even focusing of the incident beam is not necessary.

In the present paper, the roughness of the side walls of nanowires prepared by SPNI is discussed quantitatively, leading to the estimates of the line-width roughness originated from the polymer molecule used. The intrinsic cylinder-like shape of the nanowire allows direct observation of the side walls by scanning probe microscopy, allowing observation of the shapes of the polymer molecules. To discuss only the effects of shapes of molecules and cross-linking reactions on the structures of nanowires, we have chosen polystyrene derivatives as the target polymer materials which are not only the typical base resin of resist materials but also the polymers with well-investigated molecular conformations, complete amorphous phase in their solid state at room temperature, and negligible main-chain scission reaction efficiency upon irradiation to radiations.

## Experimental Section

Poly(styrene)s (PS) were purchased from Aldrich Chemical Co. Ltd., or synthesized by an anion polymerization technique from the corresponding doubly distilled monomers using *n*-butyllithium as an initiator, giving polymers with monomodal molecular weight distributions and polydispersities of less than 1.2 after fractional precipitation.[12,13] The number-average molecular weights ($M_n$) of the synthesized PS varied from $5.0 \times 10^4$ to $6.25 \times 10^5$. Poly(vinylphenol) (poly(*p*-hydroxystyrene): PHS), poly(*p*-bromostyrene) (PBrS), and poly(*p*-chlorostyrene) (PClS) were purchased from Aldrich Chemical Co. Ltd.; their $M_n$ values were $1.17 \times 10^4$, $6.5 \times 10^4$, and $7.5 \times 10^4$, respectively. Thin films of polymers on a Si substrate were irradiated in a vacuum chamber ($<10^{-4}$ Pa) by 450−560 MeV $^{129}$Xe ion beams from the cyclotron accelerator at Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Research Agency. The fluence of the incident ions varied from $10^8$ to $10^{10}$ ions/cm$^2$. The irradiated polymer films were developed using tetrahydrofuran (THF) for PHS or using benzene, chlorobenzene, toluene, and cyclohexane for PS, PBrS, and PClS while 2 min at 25 °C. The sizes and shapes of the nanowires formed along particle trajectories were observed using a SPI-4000 atomic force microscope (AFM) from Seiko Instruments, Inc. The densities of the polymer films were measured by the sink-float density determination method in a methanol−dimethyl sulfoxide−carbon tetrachloride solvent mixture.

## Results and Discussion

A heavy ion particle impinging on target polymers can release high-density intermediates within a limited area around the ion projectile. Irradiation of the polymers results in a cross-linking reaction along the ion track, resulting in the formation of a cylinder-like structure (nanowire) corresponding to each ion projectile. The non-cross-linked area can then be eliminated by development with a suitable solvent for each polymer, utilizing the change in solubility induced by gelation of the polymer, so that the nanowires are completely isolated on the Si substrate. Figure 1 shows a series of AFM images of nanowires produced by 450 MeV Xe ion irradiation in thin films of PS of a variety of molecular weights. The correlation between size (radius of the nanowire cross section) and molecular weight was investigated precisely, and a clear increase in radius was observed as the molecular weight of the target polymers increased.[8,9] The averaged sizes of the nanowires were described well by the theoretical model, which considered energy distribution in the ion track, efficiency of the cross-linking reaction, and the molecular weight and backbone conformation of the target polymers, as described in our previous reports.[8,9,11] The radial dose distribution ($\rho_E(r)$ eV nm$^{-3}$) in an ion track is given as a function of radial distance from a particle trajectory ($r$ nm) by the following equation:[14]

$$\rho_E(r) = \frac{\mathrm{LET}}{2}\left[2\pi r^2 \ln\left(\frac{e^{1/2} r_p}{r_c}\right)\right]^{-1} \quad (1)$$

where LET (linear energy transfer, eV nm$^{-1}$) is the averaged energy deposition of the incident particle per unit length along the trajectory, and $r_c$ and $r_p$ are the radii of the core and penumbra areas, defined from the equipartition theorem of

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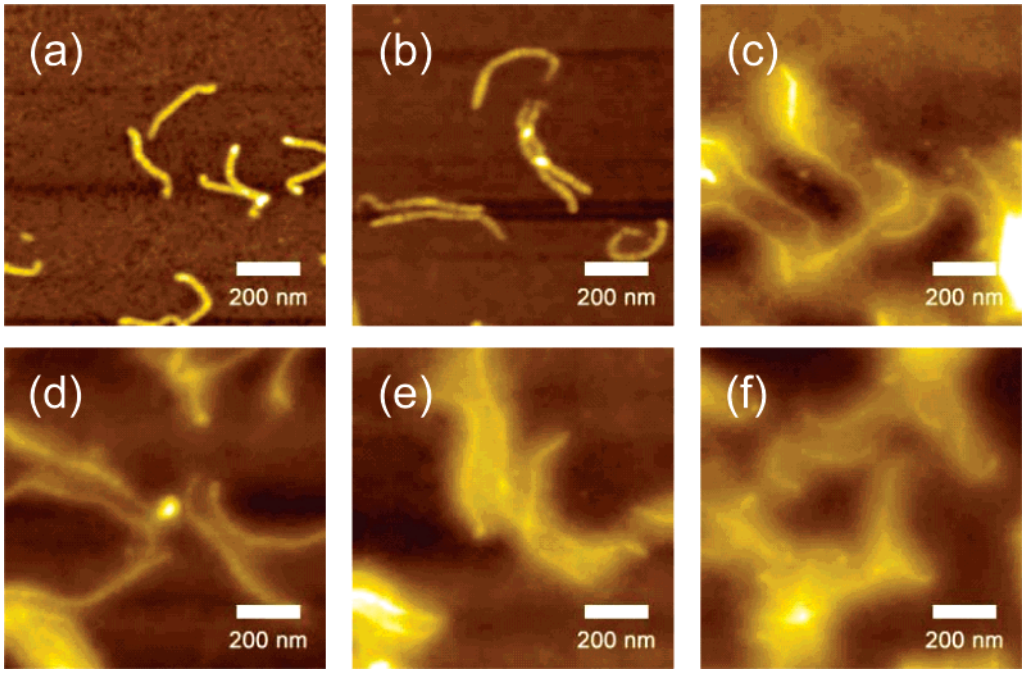


**Figure 1.** AFM micrographs of nanowires based on poly(styrene) (PS) with a variety of molecular weights, produced by the SPNI technique. The nanowires were collapsed by the development process and are observed on the substrate as "lying" wires. Images a−f were observed in thin films of PS with $M_n$ = (a) 5.0 × $10^4$, (b) 5.2 × $10^4$, (c) 1.15 × $10^5$, (d) 1.9 × $10^5$, (e) 3.5 × $10^5$, and (f) 6.25 × $10^5$. SPNI was performed using 450 MeV $^{129}Xe^{23+}$ ion beams at a fluence of (1−3) × $10^9$ ions $cm^{-2}$. Development was carried out in cyclohexane for 2 min.

collisions of charged particles with matter.[14] The gelation of the polymer materials (one cross-linking point per macromolecule) allows the derivation of energy density ($\rho_{cr}$ eV $nm^{-3}$) at the boundary of an ion track as a function of cross-linking efficiency ($G(x)$ (100 eV)$^{-1}$: number of cross-links induced by a radiation-deposited energy of 100 eV):[11]

$$\rho_{cr} = \frac{100\rho A}{G(x)mN} \tag{2}$$

where $A$ is Avogadro's number, $m$ is the mass of a monomer unit, $\rho$ (g $nm^{-3}$) is the density of the polymer, and $N$ is the degree of polymerization. Thus, the theoretical estimate of $r$ is given by substitution of $\rho_E$ with $\rho_{cr}$ as follows:[10]

$$r^2 = \frac{\mathrm{LET}G(x)mN}{400\pi\rho A}\left[\ln\left(\frac{e^{1/2}r_p}{r_c}\right)\right]^{-1} \tag{3}$$

The radii of the poly(styrene)-based nanowires were 12.8, 14.6, 22.9, 28.5, 45.7, and 62.5 nm for poly(styrene)s with molecular weights of 5.0, 5.2, 11.5, 19.0, 35.0, and 62.5 × $10^4$, respectively. These values are in good agreement, within an error margin of 12%, with those obtained using eq 3, with the following empirical parameters: LET = 1.0 × $10^4$ eV $nm^{-1}$ (calculated for 450 MeV Xe ions in poly(styrene) by the Monte Carlo simulation code "SRIM 2003"[15]), $G(x)$ = 0.10 (100 eV)$^{-1}$,[16] $\rho$ = 1.05 g $cm^{-3}$, and $m$ = 104 g $mol^{-1}$. Figure 2 shows AFM images of the nanowires formed in all polystyrene derivatives. The nanowire radii of these polystyrene derivatives are summarized in Table 1. The values of $G(x)$ for PClS and PBrS were reported as 0.30−1.6 (100 eV)$^{-1}$, which were considerably higher than that of PS.[17] In the case of polystyrene derivatives, it was reported that $G(x)$ showed considerable decrease upon heating of the materials higher than ∼340 K. It should be noted that the local heating of the polymer material within an ion track may cause a decrease in $G(x)$. On the basis of simulated values of LET for the polystyrene derivatives (LET = (1.12−1.2) × $10^4$ eV $nm^{-1}$) and an assumption of $G(x)$ = 0.5 (100 eV)$^{-1}$ for all derivatives, the values of $r$ calculated for PClS, PHS, and PBrS were 30, 10, and 21 nm, respectively, which is in good agreement with the values estimated by direct AFM observation (Table 1). The efficiency of main chain scission ($G(s)$ (100 eV)$^{-1}$: number of main-chain scission induced by a radiation-deposited energy of 100 eV) should be considered as the parameters determining $r$; however, the polystyrene derivatives used in the present study had been

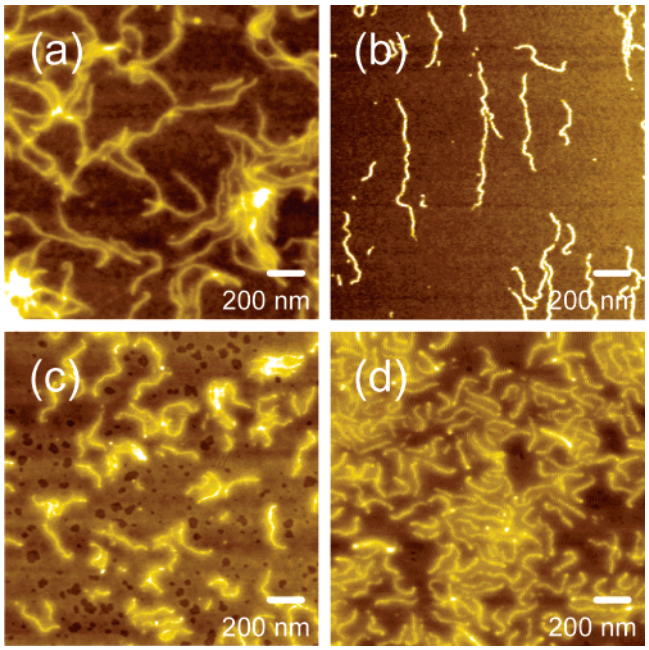


**Figure 2.** AFM micrographs of nanowires produced by the SPNI technique using polystyrene derivatives. Images a−d were observed in thin films of (a) poly(styrene) (PS), (b) poly(vinylphenol) (PHS), (c) poly(*p*-chlorostyrene) (PClS), and (d) poly(*p*-bromostyrene) (PBrS). SPNI was performed using 560 MeV $^{129}Xe^{26+}$ ion beams at a fluence of (1−8) × $10^9$ ions $cm^{-2}$. Development was carried out in cyclohexane (for PS), THF (for PHS), or benzene (for PClS and PBrS) for 2 min.

CDV

**Table 1. Molecular Weights of Polystyrene Derivatives, Roughness of Nanowires, and Conformation Parameters**

| | $M_n$ ($\times 10^4$) | $M_w/M_n$ | $r$ (g cm$^{-3}$) | $r$ (nm) | $\sigma^a$ (nm) | $\sigma_C{}^b$ (nm) | $C_\infty{}^c$ | $a^c$ (nm) |
|---|---|---|---|---|---|---|---|---|
| PS | 5.0 | 1.06 | 1.05 | 12.8 | 2.5 | 2.5 | 10.8 | 1.1 |
| PClS | 7.5 | 1.10 | 1.22 | 31.2 | 7.1 (7.9) | 4.7 | 11.1 | 1.6 |
| PHS | 1.17 | 1.21 | 1.17 | 10.9 | 1.4 | 4.3 | 12.0 | 1.58 |
| PBrS | 6.5 | 1.13 | 1.28 | 18.7 | 6.6 (7.9) | 5.3 | 12.5 | 1.76 |

[a] Width roughness determined for nanowires developed using benzene (for PS, PClS, and PBrS) or THF (for PHS). Values in parentheses are determined for development with chlorobenzene. [b] Calibrated roughness of the nanowires at $M_n = 5.0 \times 10^4$ for all polystyrene derivatives. [c] Conformation parameters: $C_\infty$ and $a$ are the characteristic ratios of the polymer chains and the Kuhn segmentation lengths of the polystyrene derivatives in the solutions used for the development procedure. The parameters are cited from ref 22.

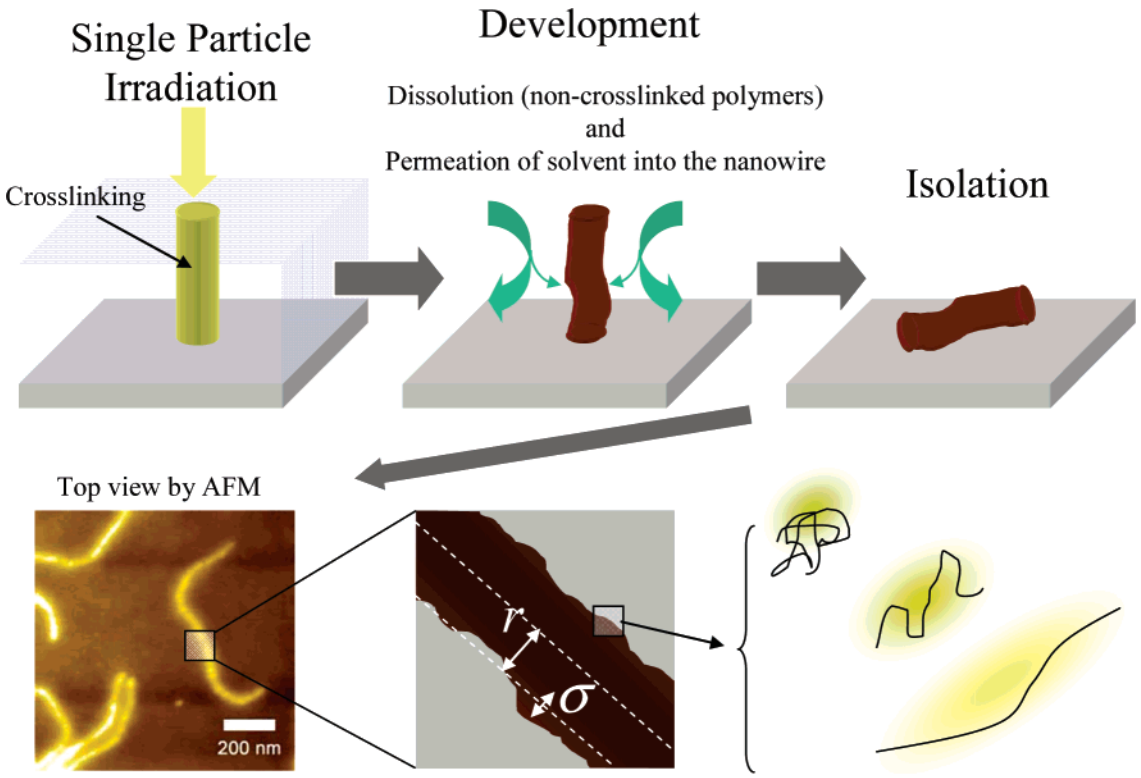


**Figure 3.** Schematic procedure for the SPNI technique and methods of determination of cross-sectional radius ($r$) and width roughness ($\sigma$).

reported to show extremely low $G(s) < 0.02$ (100 eV)$^{-1}$ in comparison with their $G(x)$.[16,17] This is the case giving good estimates of $r$ by eq 3 without consideration of $G(s)$.

Because the present technique gives the negative tone of the cross-linked nanowires without any acid catalytic reactions, the effects of development procedures, acid diffusion, etc., can be eliminated from possible factors causing an increase in width roughness. Because one nanowire is produced by a single particle in the present technique, we can also neglect the effect of spatial focusing and scattering on roughness. The production of one nanowire using the corresponding charged particle is illustrated schematically in Figure 3. The origin of roughness, therefore, is predicted to be the "shape" (conformation) of the target polymer chains because the effects of molecular weight and radial dose distribution have already been taken into account in the size of the nanowire, as shown by the good correlation between $r$ and $N$ or $\rho_E$.

Figure 4 shows the thickness distribution of nanowires based on PS with a variety of molecular weights. The distribution of $r$ increases considerably with an increase in molecular weight. The value of width roughness was defined as the standard deviation ($\sigma$) of $r$, as presented in Figure 4. The statistical limit of error was suppressed at values lower than 3.0% for all deviation analyses. Figure 5 shows the dependence of $\sigma$ on the degree of polymerization ($N$: number of monomer units in

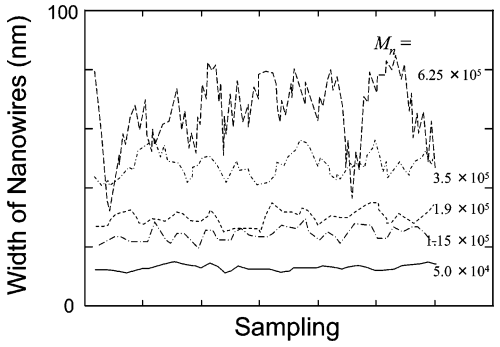


**Figure 4.** Variation of $r$ in poly(styrene) nanowires produced by SPNI with 450 MeV $^{129}Xe^{23+}$ ion beams.

polymer chains) of PS. According to the statistical theory on the conformation of polymer chains, the gyration radius ($R_g$) of polymer molecules is determined by following formula, using an impermeable rigid-body approximation and the Mark–Houwink equation:[18]

$$a\sigma = R_g = \kappa M^\nu = \kappa\left(\frac{N}{M_m}\right)^\nu \qquad (4)$$

where $a$ is a scaling factor, $M_m$ denotes the mass of a polymer chain unit, and $\kappa$ is a constant. The correlation represented in

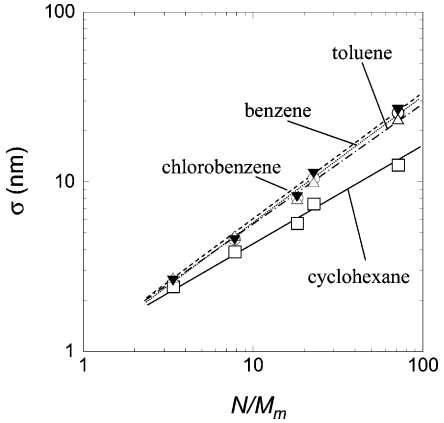


**Figure 5.** Correlation between the degree of polymerization ($N$) and the observed width roughness ($\sigma$) of poly(styrene) nanowires. Squares (solid line), circles (dotted), open-triangles (dot−dashed), and closed-triangles (dashed) represent values of roughness recorded after development with cyclohexane, benzene, toluene, and chlorobenzene, respectively.

Figure 5 is well described by eq 4, giving a value for the index $\nu$ of 0.76 in the case of development by benzene. The observed value of $\nu$ is close to the upper limit of $\nu = 0.8$, which should be observed for completely expanded chains. This is due to contact with a "good" solvent (toluene for PS) for the polymer during the development procedure. The observed values of $\nu$ for nanowires developed by toluene and chlorobenzene are 0.70 and 0.76, respectively. A light-scattering experiment with atactic poly(styrene) solution in these solvents produced values of $\nu$ as follows: ~0.74 in benzene,[19] 0.69−0.75 in toluene,[20,21] and 0.75 in chlorobenzene,[22] which are consistent with the values obtained in the present study. In contrast to these "rich" solvents, cyclohexane is often the solvent of choice for atactic poly(styrene), which has a $\theta$ temperature of around 34.5 °C.[23,24] Nanowires developed by cyclohexane showed a considerable decrease in the value of $\nu$, which was observed to be 0.54; this value is consistent with the value of $\nu$ in cyclohexane solution systems ($\nu = 0.50$).[23,24] This relatively poor solvent for poly(styrene) causes shrinking of the molecules during the development process, leading to a lower dependence of $\sigma$ on chain length. The scaling factor $a$ was also determined as 0.8−1.1 for all solvents used. The clear correlation between $\sigma$ and $N$ (or between $\sigma$ and $R_g$ with $a \approx 1$), as represented in eq 4, suggests that the actual gyration radius ($R_g$) of the polymer molecules during development in the solvent is *memorized* on the substrate even after the drying process as the absolute value of standard deviation ($\sigma$). For PClS and PBrS, benzene is a relatively poor solvent compared with chlorobenzene and toluene. As seen in Table 1, development with chlorobenzene causes a considerable increase in the $\sigma$ value of nanowires based on both PClS and PBrS. This is supported by the fact that PClS and PBrS show higher values of $\nu$ in chlorobenzene ($\nu = 0.8$[25] and 0.69[22]) than in benzene ($\nu = 0.56$[26] and 0.53[27]).

The empirical correlation of eq 4 allows estimates of the value of $\sigma$ at a constant polymer chain length. To compare the absolute size of polymer molecules with certain chain length, the values of $\sigma$ are calibrated at a molecular weight of $5.0 \times 10^4$ and summarized as $\sigma_C$ in Table 1. The stretched chain length of the polymer with $M_w = 5.0 \times 10^4$ is estimated as ~50 nm based on the C−C bond length of 0.16 nm and the tetrahedral coordination of carbon atoms in the PS backbone. The value of $\sigma_C$ (or $R_g$) of PS in the present study is far smaller than the stretched chain length, suggesting that the backbone is taking the entangled wormlike form as in the solution. This is also supported by the fact that the value of $\sigma_C$ (or $R_g$) is considerably larger than the persistence length in the PS backbone (0.6−0.7 nm), which certifies the applicability of wormlike chain model via the so-called "scaling law" of macromolecular chain conformation.[18]

On the basis that the wormlike chain model in solution is a good approximation for estimates of roughness, the characteristic ratios ($C_\infty$, representing the polymer backbone rigidity) of the polymer chains in the solvents used for the development procedure are given as 10.8, 11.1, 12.0, and 12.5 for PS, PClS, PHS, and PBrS, respectively.[22] The values of $C_\infty$ show a striking contrast to the values of $\sigma$, thus showing direct experimental evidence of the clear quantitative correlation between the width roughness of the nanowires and the backbone conformation of the polymers in the resist materials. The empirical correlation between $\sigma$ and $N$ also gives estimates of $\sigma$ for polystyrene derivatives with a variety of molecular weights. For poly(styrene) with $M_n = 1.0 \times 10^4$ developed with cyclohexane, the width roughness is calculated as $\sigma = 1.0$ nm. This value implies the maximum contribution to roughness from the molecular conformation of poly(styrene). Thus, if larger values of roughness are observed in the nanolithography process, we should consider factors other than the molecular conformation of the polymers.

## Conclusion

A quantitative correlation was found between the conformation of polymer molecules and the roughness of nanowires formed by the SPNI process from polystyrene derivatives. The roughness showed a clear increase with the molecular weight of the poly(styrene), which was described well by the Mark−Houwink equation. The index value in the equation was found to depend strongly on the solvents used in the development procedure. Nanowires based on poly(styrene) show indexes of $\nu = 0.70-0.76$ (development by benzene, toluene, and chlorobenzene) and 0.54 (cyclohexane). The indexes are quite consistent with the values of poly(styrene)s estimated by the light scattering experiments in the corresponding solvents, suggesting that the gyration radius of the polymer molecules contributes to the width roughness of nanowires. The actual gyration radius in the solvent is *memorized* on the substrate even after the drying process as the absolute value of standard deviation of the nanowire width. The present results also enable us to predict pattern roughness originating from the conformations of the polymer molecules used in the lithography process.

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