# Microscopic Deformation Process in Poly(4-methylpentene-1) under Uniaxial Tensile Stress

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ABSTRACT: Brillouin scattering (BS) and small and wide angle X-ray scattering (SAXS and WAXS) experiments were conducted on poly(4-methylpentene-1) over a wide temperature range from 16 to 85°C to investigate the microscopic deformation process in semi-crystalline polymers. It was clarified that application of uniaxial tensile stress, submicrocracks were generated in an amorphous region, resulting in a decrease in the elastic modulus along the tensile direction. The concentration of submicrocracks depended greatly on the strain level and testing temperature. It was particularly noted that submicrocracks were formed even above the glass transition temperture $(T_g)$. This implies that the molecular motion in the amorphous region above $T_g$ is partially restricted by the presence of the crystalline region. WAXS experiments showed that, with increasing applied strain, the strain of the crystal lattice increased at an initial stage, and then decreased slightly when a rapid increase in the submicrocracks concentration occurred. These results suggest that the microscopic deformation in semi-crystalline polymers proceeds under the mutual influence of and intimate correlation between the amorphous and crystalline phases.
  KEY WORDS    Poly(4-methylpentene-1) / Brillouin Scattering / Small and Wide Angle X-Ray Scattering / Submicrocracks / Microscopic Deformation / Uniaxial Tensile Stress /

It is of importance to investigate the deformation and fracture mechanism of polymers from a microscopic viewpoint. Recently, we investigated the microscopic deformation process under uniaxial tensile stress in a few glassy polymers such as poly(methyl methacrylate), polycarbonate and poly(ethylene terephthalate) using several methods (Brillouin scattering (BS), ultrasonic, acoustic emission (AE) and small angle X-ray scattering (SAXS)).[1-3] In these experiments, the nucleation of submicrocracks (several hundred angstrom) was detected at a low strain level before the appearance of visible crazes. The results suggested that the formation of submicrocracks reduces the elastic modulus along the tensile direction and that the concentration and shape of the submicrocracks

affect the deformation and fracture characteristics such as brittleness or ductility. Furthermore, it was confirmed from time dependent SAXS measurements that the formation of such submicrocracks is also responsible for non-linear viscoelastic phenomena such as the stress relaxation process in glassy brittle polymers.[4,5] In short, the origins of stress relaxation and recovery under large deformation come mainly from the formation and extinction process of submicrocracks, respectively.

For crystalline polymers such as polyethylene, extensive studies have been conducted by many investigators[6-8] on the deformation process of lamella and spherulites, and the detailed mechanism for the rearrangement and orientation of molecular chains has been

elucidatea. On the microscopic deformation process in semi-crystalline polymers, only a few studies have been performed mainly because of experimental difficulties. Kuksenko *et al.*[9,10] reported the formation of submicrocracks for several polymers under load and discussed the correlation between the concentration of submicrocracks and cracks or fracture initiation. Wendorff[11,12] performed SAXS experiments on polyoxymethylene samples with various mechanical and thermal history and investigated the mechanism of submicrocrack formation. In these studies, however, little attention was paid to the contribution of amorphous and crystalline regions to macroscopic deformation and the interaction between them.

In this study, BS, SAXS and WAXS measurements were carried out on a transparent semi-crystalline polymer, poly(4-methylpentene-1) (P4MP1), over a wide temperature range to examine the role of amorphous and crystalline phases in micro- and macroscopic deformation processes and the effect of $T_g$. Since the nucleation and development of heterogeneous structures such as submicrocracks reflect very sensitively the change in elastic modulus,[13] an acoustoelastic study was conducted under tensile stress using the BS technique only on optically transparent materials. P4MP1

$$(\text{\text+CHCH}_2\text{CH(CH}_3)_2\text{CH}_2\text{\text+}_n)$$
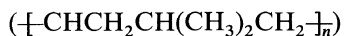
has exceptionally high transparency in spite of its rather high crystallinity, since the density of the crystalline phase is almost the same as that of the amorphous phase due to the existence of an extremely large bulky side group.[14] Since the electron density variation at the boundary between the crystalline and amorphous regions is also quite small, no peaks originating from lamella long periods could be detected. Moreover, the fact that the $T_g$ of this polymer is near room temperature $(T_g=25°C)$[14] facilitated our study of the effect of temperature, especially $T_g$, on the deformation process.

## EXPERIMENTAL

The P4MP1 used in our experiments was supplied by Mitsui Petrochemical Industries Ltd. in sheet form 2 mm in thickness and had high optical transparency and surface smoothness. X-Ray photograph showed no molecular orientation to exist. The sheets were cut into dumbbell-shaped specimens 6 mm in gauge width and 30 mm in gauge length. The degree of crystallinity was 46% as determined by X-ray measurement.

Macroscopic stress-strain curves were measured at different temperatures using the tensile machine driven by a stepping motor. The strain rate was about 10%/min. As illustrated schematically in Figure 1, the machine was secured to the X-ray measuring apparatus and the specimen was stretched in both directions in a temperature-control cell, so that an X-ray incident beam remained at the center of the specimen during deformation. Stress was monitored with strain gauges and the strain was increased stepwise during the SAXS and WAXS experiments.

BS experiments were performed using an argon ion laser (NEC model GLS-3200) operating in the polarized single mode at 514.5 nm and DAS-1 system (Burleigh Co.). A triple pass Fabry–Perot interferometer provided enough contrast to accurately determine
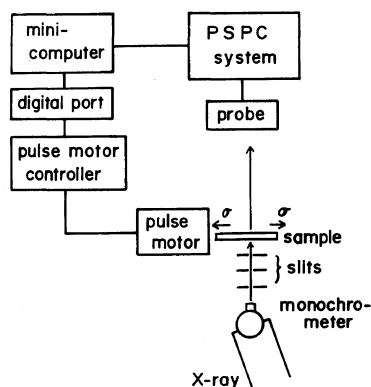


**Figure 1.** Block diagram of apparatus for small and wide angle X-ray scattering.

the position of weak Brillouin peaks. The specimen was mounted on a tensile machine inclined at an angle of 45° to the laser beam, and the scattering angle was 90°. By this scattering geometry, the hypersonic sound velocity ($V$) was obtained from the simple relation $V = f_s \lambda / \sqrt{2}$, where $f_s$ and $\lambda$ are the frequency of the Brillouin shift and laser wavelength, respectively. Detailed descriptions on the BS experiments are given in previous papers.[15,16]

Both the SAXS and WAXS measurements were conducted with a position sensitive proportional counter (PSPC) system driven by a minicomputer, as schematically shown in Figure 1. A monochromatic $CuK_\alpha$ radiation through a three slits collimating system was used as the X-ray source. The concentration of submicrocracks was determined by analyzing the SAXS profiles based on the Guinier method.[17] Other details on the scattering geometry and data analysis are presented in the previous paper.[1] WAXS measurements were performed to measure the lattice strain in the crystalline region, and the peak shift of the (200) reflection of tetragonal structure was followed with increasing strain.

## RESULTS

### Stress-Strain Relationship

The macroscopic mechanical behavior of P4MP1 was examined at different temperatures, and the observed stress-strain curves are shown in Figure 2. At 16°C, the polymer was quite brittle and fractured at $\varepsilon \simeq 5$—6% under macroscopic (nominal) strain. At 38°C and 85°C, both higher than $T_g$ ($= 25°C$), it became ductile and ruptured at $\varepsilon \simeq 60\%$. In this case, stress whitening was observed above a strain of about $\varepsilon \simeq 5\%$, roughly corresponding to the yield point, and the specimen lost its transparency. However, no appreciable necking was observed even at very high strain levels.
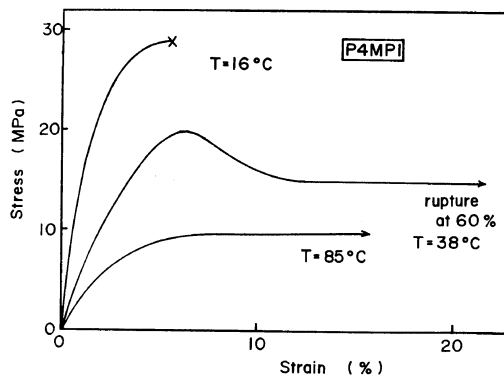
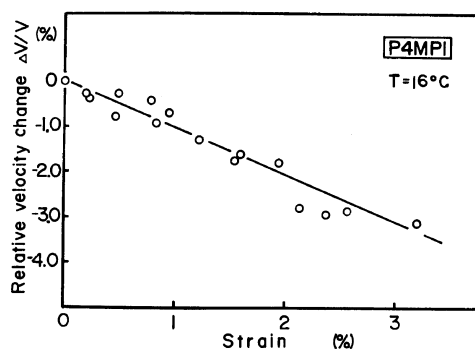**Figure 2.** Nominal stress-strain curves for P4MP1 at different temperatures.

**Figure 3.** Strain dependence of relative change in thermal phonon velocity along the stress direction at 16°C.

### Brillouin Scattering (BS)

Figure 3 shows typical results from the peak shift in the Brillouin spectra at 16°C. In the figure, only the sound velocity of the thermal phonon parallel to the stress direction is plotted as a function of applied strain, revealing that the modulus of the specimen became lower. The sound velocity of a longitudinal wave is in general proportional to the square root of the longitudinal modulus. It should be noted here that such softening could be detected even at the initial stage of strain where the stress-strain curve was almost a straight line. As suggested in previous studies[1] and discussed later in the SAXS section, this softening is attributed to the generation of certain heterogeneous structures in the specimen under a tensile load. It is also reasonable that

these locally softened parts (submicrocracks) are formed preferentially in the amorphous region rather than the more orderd and hard crystalline region. The degree of softening is almost comparable to the case of poly(methyl methacrylate), but much larger than that of ductile polymers such as polycarbonate and poly(ethylene terephthalate). Thus, the formation of submicrocracks may depend on the brittleness or ductility of specimens in some way.

## Small Angle X-Ray Scattering (SAXS)

To ascertain directly the generation of heterogeneous structures and evaluate qualitatively their concentration, SAXS measurements were performed with the tensile direction parallel to the measuring direction of the scattering profile in the PSPC probe. Typical Guinier plots at 38°C and different strains are shown in Figure 4. The central diffuse scattering negligible at low strain grew sharply above $\varepsilon \simeq 5\%$. And was considered due either to the heterogeneities (submicrocracks) or to two-phase structures resulting from an increase in density difference between amorphous and crystalline phases on stretching. Such a five-order increase in SAXS intensity cannot be explained solely by density contrast. Miyasaka et al.[18] reported the long period structure to be formed only when P4MP1 was annealed at high temperatures above ca. 180°C. In our experiments, the samples were assumed to contain no well-developed lamella and/or spherulites structures, since they had not been annealed. This scattering thus seems due to the formation of submicrocracks.

The concentration of submicrocracks estimated from the intensity at $\theta = 0°$ in the Guinier plots is shown in Figure 5 so as to indicate the strain dependence of the total submicrocrack concentration parallel to the stress direction at different temperatures. At 16°C, the central scattering intensity was detectable from about $\varepsilon \simeq 3\%$, and the sample broke at $\varepsilon \simeq 9\%$ before saturation of the sub-
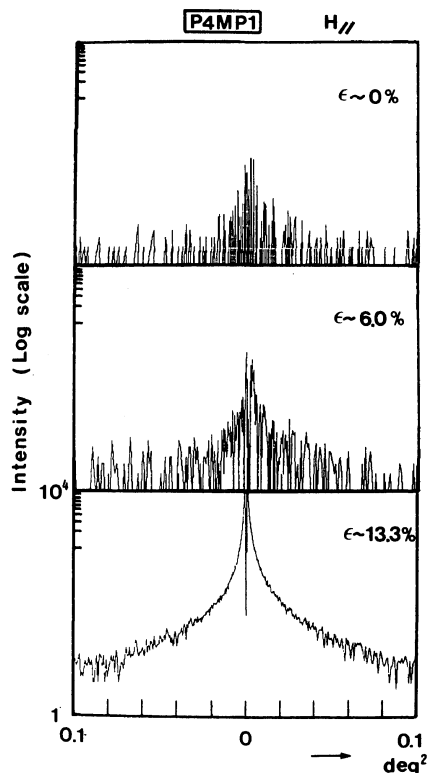


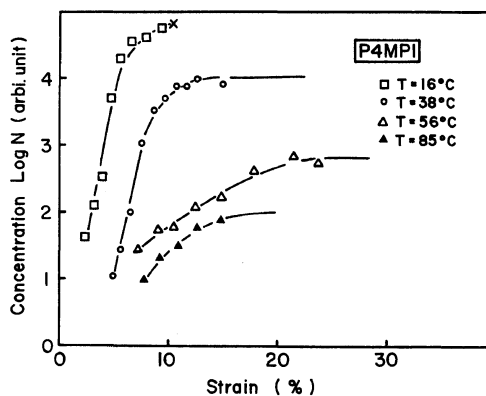**Figure 4.** Typical Guinier plots at several strain levels at 38°C.



**Figure 5.** Strain dependence of submicrocrack concentration at different temperatures.

microcrack concentration. Although the softening phenomenon in the modulus was observed in the BS experiment, submicrocrack detection by SAXS was difficult at low strain levels. At 38°C, diffuse scattering was detect-
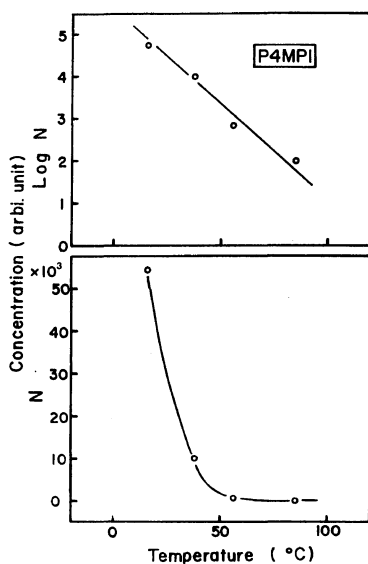
Figure 6. Temperature dependence of submicrocrack concentration at saturation plotted on log and linear scales.



Figure 7. Strain dependence of lattice strain of $a$-axis and relative intensity of (200) reflection at 16°C.



Figure 8. Strain dependence of lattice strain of $a$-axis and relative intensity of (200) reflection at 38°C.

able from about $\varepsilon \simeq 5\%$ and increased rapidly with strain. Submicrocrack concentration was saturated at $\varepsilon \simeq 10\%$ and almost constant until the rupture point at $\varepsilon \simeq 60\%$. At 56 and 85°C (far exceeding $T_g$), diffuse scattering was observed contrary to our expectation. However, it was nearly three-order less than that at 16°C.

Figure 6 shows the temperature dependence of the submicrocrack concentration at saturation or just before the fracture. The upper figure is drawn on a log scale, while the lower one is a linear scale. The submicrocrack concentration decreased almost exponentially with increasing temperature, becoming extremely low at temperatures higher than $T_g$. This suggests that submicrocrack formation is closely related to the mobility of molecular chains in the amorphous region.

*Wide Angle X-Ray Scattering (WAXS)*

WAXS measurements were conducted in order to examine how deformation proceeds in the crystalline phase. The (200) reflection was employed as a target peak because of its high
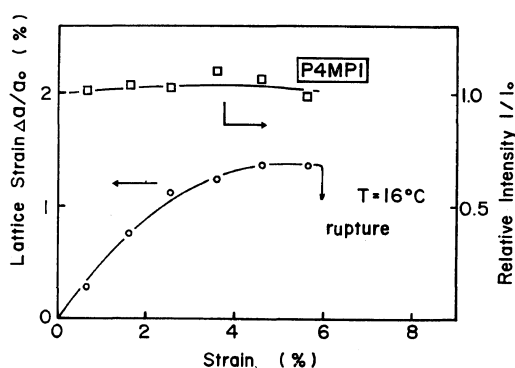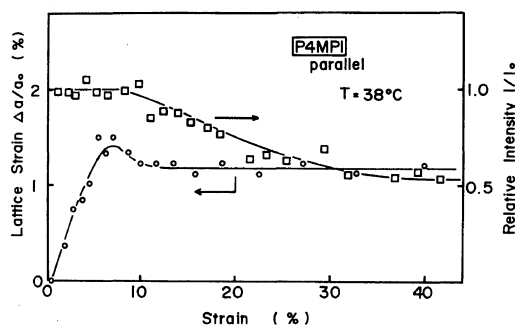
intensity and sharpness. Figure 7 shows the macroscopic strain dependence of the lattice strain of a-axis ($\Delta a/a_0$) and the relative intensity of (200) reflection ($I/I_0$) at 16°C, where $a_0$ and $I_0$ are the lattice strain and intensity of (200) reflection at zero strain, respectively. The lattice strain increased linearly at low strain and deviated from linearity at $\varepsilon \simeq 3\%$. The fracture took place at a strain level below *ca.* $\varepsilon \simeq 10\%$ and the intensity of (200) reflection was almost constant up to the rupture point.

At 38°C, the lattice strain also increased linearly at low strain and the deviation point from linearity was about $\varepsilon \simeq 5\%$, as shown in Figure 8. On further increasing the macroscopic strain, it became maximum, dropped and then was constant up to the rupture point ($\varepsilon \simeq 60\%$) irrespective of the continuous increase in macroscopic elongation. The lattice

strain was much smaller than the macroscopic strain. Most of the macroscopic elongation may thus occur in the amorphous region. The intensity of (200) reflection peak was constant up to $\varepsilon \simeq 10\%$ and then decreased gradually, indicating the possibility of molecular orientation. However, fiber X-ray photographs taken under similar conditions showed no detectable change in molecular orientation except just before the fracture. Although the lattice strain was recoverable over a whole strain region releasing the applied stress, the reflection peak intensity did not recover when the initially applied strain exceeded $\varepsilon \simeq 10\%$. The crystalline lattice itself may respond elastically with stress change, but the crystal boundary tends to deform plastically and/or collapse above $\varepsilon \simeq 10\%$, thus causing irreversible change in the intensity of the reflection peak. It should also be noted that these WAXS results show good correlation with those in SAXS at 38°C. That is, the deviation point of the lattice strain from linearity coincided with the point at which the heterogeneities became detectable by SAXS. The amplitude of the lattice strain decreased slightly when the SAXS intensity increased rapidly. Moreover, the lattice strain became constant and the intensity of the (200) reflection decreased gradually when the submicrocrack concentration attained saturation.

When the temperature was considerably higher than $T_g$ (90°C), the lattice strain was small (below $\varepsilon \simeq 1\%$) compared with that at 16 or 38°C at the same macroscopic strain. However, the intensity of the (200) reflection peak decreased gradually as did at 38°C. The former can be easily understood by assuming most of stress to be supported mainly in the amorphous region, causing a uniform flow or plastic deformation, at high temperatures.

## DISCUSSION

From these results of BS, SAXS and WAXS, the following deformation process is proposed for this semi-crystalline polymer, P4MP1. At a temperature lower than $T_g$ (16°C), the fracture occurred before the submicrocrack concentration attained saturation and the lattice strain in the crystalline part started to retreat. Because of the limited deformability in the amorphous molecular chains, the accumulation of a large number of submicrocracks tended to develop easily into visible crazes or macroscopic cracks.

When temperature is slightly higher than $T_g$ (38°C), the molecular chains in the amorphous phase become deformable to some extent and application of stress, molecular chain extension occurs locally to give rise to an embryonic state of submicrocracks. With a further increase in strain ($\varepsilon \simeq 5\%$), this embryonic state develops and is converted into submicrocracks detectable by SAXS. That submicrocracks may be formed in the amorphous region even above $T_g$ is a possibility that cannot be ruled out since amorphous chains are not able to move about freely owing to the existence of the crystalline region. The lattice strain retreats backward slightly because of the partial release of microscopic stress due to the rapid increase in submicrocrack concentration. Following submicrocrack concentration saturation, the crystal structure itself starts to deform irreversibly with a further increase in strain. Saturation is probably caused by the preventive action of microshear bands developed among the submicrocracks.[19-24]

These microscopic changes are also reflected in macroscopic mechanical behavior. In Figure 2, the nominal stress-strain curve at 38°C exhibits a considerable falling of the macroscopic stress from $\varepsilon \simeq 7\%$ to 10%. This is considered related to the decrease in the modulus due to extensive formation of submicrocracks rather than macroscopic dimensional change, since this material showed no necking throughout the entire strain region.

At temperatures much higher than $T_g$ (56 or 85°C), deformation seems to be governed primarily by the uniform flow and plastic defor-

mation in the amorphous region. Thus hardly any submicrocracks are formed, as indicated by the SAXS results. The lattice strain also becomes quite low since the uniform flow of the amorphous chains rapidly lessens the stress.

We suggest submicrocracks are formed even above $T_g$ and are important to the deformation process in semi-crystalline polymers and that amorphous and crystalline phases strongly influence each other.

## REFERENCES

1. S. Shichijyo, S. Shirouzu, S. Taki, K. Matsushige, and T. Takemura, *Jpn. J. Appl. Phys.*, **22**, 1315 (1983).
2. S. Shichijyo, K. Nishimura, S. Shirouzu, K. Matsushige, and T. Takemura, *Jpn. J. Appl. Phys.*, **23**, 846 (1984).
3. S. Shirouzu, S. Shichijyo, S. Taki, K. Matsushige, K. Takahashi, and T. Takemura, *Polym. J.*, **16**, 223 (1984).
4. S. Shichijyo, K. Matsushige, and T. Takemura, *Jpn. J. Appl. Phys.*, **23**, L218 (1984).
5. S. Shichijyo, K. Matsushige, and T. Takemura, *Rep. Prog. Polym. Phys. Jpn.*, **27**, 341 (1984).
6. T. Hashimoto, A. Todo, Y. Tsukahara, and H. Kawai, *Polymer*, **20**, 642 (1979).
7. T. Kyu, N. Yasuda, S. Suehiro, T. Hashimoto, and H. Kawai, *Polymer*, **21**, 1205 (1980).
8. V. I. Gerasimov, Yav. Genin, and D. Ya. Tsvaankin, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2035 (1974).
9. V. S. Kuksenko, V. S. Ryskin, V. I. Betekhtin, and A. I. Slutsker, *Intern. J. Fracture*, **11**, 629 (1975).
10. V. S. Kuksenko and V. P. Tamuzs, "Fracture Micromechanics of Polymer Materials," Martinus Nijhoff Publishers, Haugue, 1981.
11. J. H. Wendorff, *Prog. Colloid Polym. Sci.*, 135 (1979).
12. J. H. Wendorff, *Polymer*, **21**, 553 (1980).
13. B. C. Yap, S. Shichijyo, K. Matsushige, and T. Takemura, *Jpn. J. Appl. Phys.*, **21**, L523 (1980).
14. B. Hartmann, *J. Appl. Phys.*, **51**, 310 (1980).
15. B. C. Yap, S. Shichijyo, K. Matsushige, and T. Takemura, *J. Appl. Phys.*, **54**, 5456 (1983).
16. S. Shichijyo and T. Takemura, *Mol. Cryst. Liq. Cryst.*, **78**, 251 (1981).
17. A. Guinier and G. Fournet, "Small Angle Scattering of X-Rays," John Wiley, London, 1955.
18. T. Tanigami and K. Miyasaka, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1865 (1981).
19. C. B. Bucknell, D. Clayton, and W. E. Keast, *J. Mater. Sci.*, **7**, 1443 (1972).
20. M. Higuchi and H. Ishii, *Rep. Res. Inst., Appl. Mech., Kyushu University*, **16**, 69 (1968).
21. K. Matsushige, S. V. Radcliffe, and E. Baer, *J. Mater. Sci.*, **10**, 833 (1975).
22. R. P. Kambour, *J. Polym. Sci., Macromol. Rev.*, **7**, 1 (1973).
23. S. B. Newman and I. Wolock, *J. Res. Natl. Bur. Stand.*, **58**, 339 (1957).
24. G. Jacoby and C. Cramer, *Rheol. Acta*, **7**, 23 (1968).