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Origin of High Elastic Recovery of Hard-elastic Polypropylene Film at Room Temperature: the Mixed Contribution of Energy Elasticity and Entropy Elasticity

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 Electronic Supplementary Information

Abstract The crystalline and amorphous regions were alternately arranged in the hard elastic polypropylene (PP) films with row-nucleated lamellae. In this work, their structure evolution during stretching and recovery at room temperature was followed and the elastic recovery mechanism was discussed by twice cyclic tensile experiment. During the first stretching to 100%, the lamellae crystals are parallel separated and the intercrystallite crazing is formed at the first yield point. Many nano-cavities within the intercrystallite crazing appear when the strain reaches 20%. The strain-hardening process accompanies with the lamellae long period increasing and the intercrystallite crazing enlargement. After the secondary yield point, the lamellae cluster is further separated and more nano-cavities appear. The first and second recovery processes are complete overlap. During recovery, firstly, the energy elasticity provided by nano-cavities surface tension drives the shrinkage of material, and then the entropy elasticity related to amorphous chain relaxation plays a leading role when the strain is smaller than the secondary yield point. The elastic recovery process of hard elastic material is the co-contribution of energy elasticity and entropy elasticity. This work gives a clearer recognition about the source of hard elastic property and the role of amorphous region in material's deformation.

Keywords Hard-elastic material; Elastic recovery; Entropy elasticity; Energy elasticity

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INTRODUCTION

The hard-elastic materials show a pronounced difference in mechanical properties compared with those with spherulite.^[1] They exhibit high elastic recovery at large strain in a wide temperature range.^[2,3] Many experimental results have confirmed that these interesting properties are attributed to the special crystalline structure, which is oriented perpendicularly to the machine direction and formed under a shear or stretching flow field.^[1,4–11] However, up to now, the source of hard-elastic property remains controversial.

In the 1970s, some elastic models based on the elasticity deformation of row structured lamellae were built up to explain the hard-elastic mechanism during uniaxial stretching. Clark assumed that the elastic recovery came from the reversible shear deformation of lamellae crystals.^[12,13] Sprague and Noether proposed that the elastic energy induced by lamellae bending resulted in reversible recovery.^[11,14] Cannon and

Hosemann *et al.* proposed a microparacrystal model to explain the retractive process.^[1,7] However, many recent experimental data cannot support these models.^[3,9,10,15]

With the increase of the cognization of microstructure evolution on the hard-elastic materials, researchers found that their deformation behavior is always accompanied with the lamellae crystals' separation and the formation of some crazes in amorphous region.^[16,17] They believed that the amorphous region played a more important role than the crystalline region in the elastic recovery process.^[18] Park *et al.* followed the retractive force at constant strain at different temperatures. They found that this force gradually increased with the temperature decreases, indicating that the hard-elastic behavior was not only decided by the rubber-like entropic elasticity.^[2] Later, some energy elasticity models were proposed based on the hypothetical deformation of amorphous regions.^[19–22] However, these earlier energy elasticity models cannot explain the lose part of elasticity at low temperature for hard-elastic materials. Then, some researchers hypothesized an indistinct theory that the reversible force may be related to the entropy effect and the increase of surface energy induced by forming microfiber structure,^[10,23–25] but the detailed and visualized experimental data were not

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given. The energy transformation mechanism during elastic recovery was still not well understood until nowadays. Although the researchers believed that microfibrils would provide the recovery energy by their periodic appearance and vanishment,^[3,19,20] there is still no intuitive evidence that the microfibrils form when stretched at room temperature. Recently, Lin *et al.* even suggested no crazes and microfibrils formed during cyclic loading at room temperature.^[15,16] They proposed that the elastic property was determined by hyperelasticity, which was based on the micro-phase separation in the amorphous phase during the tensile. Obviously, the structure evolution of hard elastic materials in elongation and retraction process is still controversial. Whether the cavities or fibrils are formed during stretching still has some controversy. This makes the source of hard elasticity untraceable. Therefore, it is important to fully understand the structural evolution during stretching and recovery processes.

For a long time, as to the hard elastic mechanism, researchers always pay attention to the elastic characteristics under the condition of 40%–60% strain. This strain is only the strain-hardening region in the stress-strain curve during first stretching.^[2,19,26–28] But in fact, the PP hard elastic film shows high elastic recovery even at 100% strain or more. Apparently, the model based on small strain results cannot accurately describe the source of hard elastic property at large strain. In addition, the high elastic properties can occur periodically. After 100 times cyclic stretching, the hard elastic recovery is still kept over 80%. Therefore, the recovery process in the large strain cyclic load-unload experiment should be more important to understand the source of hard elastic property. Hence, in this work, *in situ* SAXS/WAXS and FTIR were used to track the microstructure evolution during two times cyclic stretching experiment. The evolution of microstructure and the role of retractive force during recovery were revealed. This work would give a clearer explanation on the structure dependence of elastic property for hard-elastic materials and the source of their high elastic recovery.

EXPERIMENTAL

Preparation of Hard-elastic Film

The PP hard elastic films were supplied by Shenzhen Senior Technology Material company, Ltd., China. The initial thickness was $14 \pm 1 \mu\text{m}$, whereas that stretched to 100% was $13 \pm 1 \mu\text{m}$. Hence, the sample thickness shows nearly no change during cyclic tensile experiment. In order to improve the hard elastic property, the films were annealed for 30 min at 145°C in a hot oven.

Cyclic Tensile Test

The Linkam TST350 equipment was used to test the mechanical properties. The strip stretching sample was 25 mm long and 10 mm wide. The stretching speed in the cyclic tensile process was 25 mm/min. The cyclic procedure was as follows, firstly stretched to strain 100% and kept for 1 min, then relaxed to the initial position, and also kept for 1 min. This process was repeated twice. Fig. 1 gives the stress-strain curve of two-time cyclic tensile experiment. Compared with the first stretching, during the second stretching, the yield strength turns smaller and the stress plateau is expanded. The first and

second recovery processes are completely overlap. In addition, the third stretching and recovery curves coincide with the second ones. Therefore, only the first two cyclic tensile curves are given in this paper.

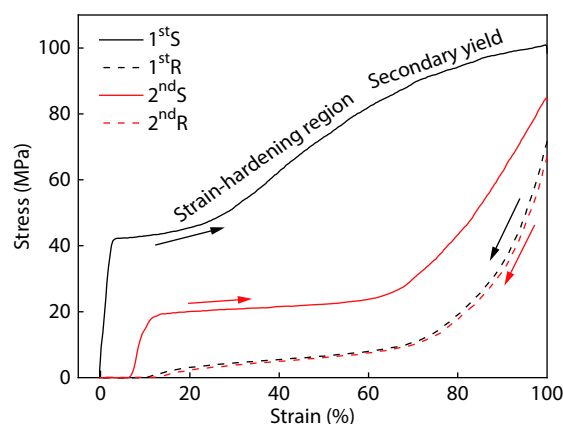


Fig. 1 The stress-strain curves of two-times cyclic tensile experiment. S means stretching and R means recovery.

In situ Small Angle X-ray Scattering (SAXS)

Two-dimensional *in situ* SAXS measurements were performed using Synchrotron Radiation Facility (Beijing, China). The sample-to-detector distance was 4995 mm for SAXS. The wavelength of X-ray radiation was 0.154 nm. During the *in situ* SAXS experiment, the Linkam TST350 equipment was set between the X-ray source and the detector. The strip stretching sample was 25 mm long and 10 mm wide. The stretching speed in the cyclic tensile process was 25 mm/min. The SAXS signals were collected when the sample was stretched to set position; after exposure for 10 s, the stretching was continued. We must point out that this stop shows no effect on the final microstructure. The stretching sample was the same size as that in the cyclic tensile experiment. The intensity profiles were obtained by integration of the 2D patterns. The long period in meridional direction (L_m) was obtained from the q_{max} according to Bragg's law:

$$L_m = 2\pi/q_{\text{max}} \quad (1)$$

where L_m is the lamellae long period.^[29]

The orientation parameters of lamella (f_l) were calculated from the full width at half-maximum (FWHM) of azimuthal integration curve for the lamella, which are defined according to Herman's function:^[15]

$$f_l = (3 \langle \cos^2 \phi \rangle - 1)/2 \quad (2)$$

In situ Fourier Transform Infrared Spectroscopy (FTIR)

In situ FTIR measurement was performed using IS-50R FTIR spectrometer (Thermal Scientific, USA). The Linkam TST350 equipment was set between FTIR source and the detector. The detector was an MCT detector and the resolution was 4 cm^{-1} . The accumulation was 4 scans.

To calculate the degree of orientation, the beam was polarized through a Spectra-Tech zinc selenide wire grid polarizer from Thermo Electron Corp. The dichroic ratio, R , was calculated by the ratio of the absorbance from beams polarized parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the machine direction. Then the data were evaluated in the degree of orienta-

tion, f :[30]

$$R = \frac{A_{\parallel}}{A_{\perp}} \quad (3)$$

$$f = \frac{R-1}{R+2} \times \frac{R_0+2}{R_0-1} \quad (4)$$

R_0 was given by:

$$R_0 = 2 \cot^2 \psi \quad (5)$$

where ψ was the angle between the polymer chain axis and the transition moment of the investigated absorption band.[30] Here, the absorption bands at 998 and the 2723 cm^{-1} were used to calculate the orientation of crystalline phase and amorphous phase, respectively.[31] ψ at 998 and 2723 cm^{-1} was 18° and 90°, respectively.[31]

2D IR Correlation Analysis

Time-resolved spectra in the range of 1250–800 cm^{-1} were first subjected to the baseline correction to minimize the effect of baseline instabilities. This data treatment was automated by the program written in the Thermo software package. Then 2D correlation analysis was performed on the difference spectra of the deformed specimens.

Stress Relaxation Test and Estimation of the Surface Energy Associated Part of Retractive Stress

To semi-quantitatively estimate the surface-energy-associated part of retractive stress, the stress relaxation curve was tested on an H&P Inspekt table blue machine. The test conditions and sample sizes are the same as above. The strain was kept at a given position and the sample was immersed in the alcohol after 1600 s keeping time. When the PP surface was wetted, the stress dropped immediately. After the alcohol evaporated from the sample, the stress came back to its initial value. According to Young-Durpe's equation:

$$r_s - r_{SL} = r_L \times \cos \theta \quad (6)$$

where r_s is the surface tension of solid PP, namely 32 dyne/cm^2 ; r_{SL} is the interfacial tension between solid PP and alcohol; r_L is the surface tension of alcohol (22.75 dyne/cm); θ is the contact angle between PP and alcohol, 39°. F_s is the surface-energy

associated to the part of retractive stress and should be proportional to r_s while ΔF is the stress reduction due to the addition of alcohol and should be proportional to $r_L \times \cos \theta$. Then F_s could be calculated by:[32]

$$F_s / \Delta F = r_s / (r_L \times \cos \theta) \quad (7)$$

RESULTS AND DISCUSSION

In situ SAXS

To track the evolution of microstructure during the cyclic stretching, the *in situ* SAXS patterns were collected and shown in Fig. 2. Before stretching, two scattering spots appear along the equatorial direction, indicating the highly oriented lamellar crystalline structure.[33] The strain of 10% is located in the yield plateau and was regarded as craze formation region in the past.[34,35] The appearance of symmetric weak meridional scattering signals closing to the beam center is related to the formation of intercrystallite crazing. Although these signals are similar to those of classical crazing (cavitation) in the semi-crystalline polymer with spherulite structure,[36,37] here the intercrystallite (delocalized) crazing is formed during stretching of hard elastic polypropylene film. This crazing mechanism is similar to that of the semi-crystalline polymer with spherulite structure stretching in active medium where lamellae in the spherulite structure were separated parallel.[38,39] Some initial intercrystallite crazing would form in the amorphous area between the lamellae clusters, since the long tie chains were stretched to be broken in distributed sparse areas during the sample elongation. The contour of the signals indicates that the intercrystallite crazing is elongated perpendicularly to the tensile direction. These signals then gradually become broadened and stronger with the strain increasing, indicating more intercrystallite crazing. Meanwhile, the lamellae signal moves towards the beamstop and the long period is increased synchronously. In the equatorial direction, a very weak scattering signal appears at strain 20% and further increases with the strain. This weak signal indicates the appearance of the nanosized cavities parallel to the tensile direction due to the

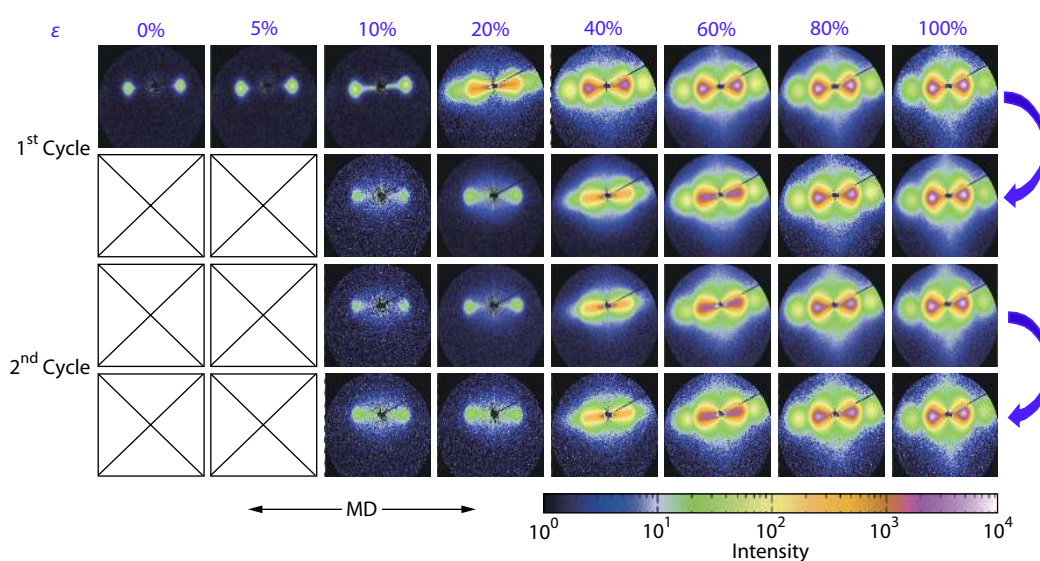


Fig. 2 SAXS patterns collected during two-times cyclic stretching of hard-elastic PP film. The tensile direction is horizontal.

broken chains. In the recovery process, most scattering signals exhibit reversible change. The lamellae signals return to initial position and some intercrystallite crazing signals are left. The weak scattering signals in the meridional direction totally disappear, meaning that the nano-cavities formed by stretching are closed. The first stretching results in some unrecoverable intercrystallite crazing in the sample, which destroy the continuity of the sample. This is also the reason why the hard elastic material could not totally recover.

The scattering signals in the second cyclic are similar to the above, indicating that the effect of left unrecoverable intercrystallite crazing on the reversible recovery is limited. The crazing signal becomes stronger after the second recovery, meaning that the intercrystallite crazing formed by the interface separation is more apparent. This irreversible interface separation leads to the decrease of elastic recovery values after multiple stretching.

To clarify the structural deformation in the cyclic stretching, the lamellae orientation degree was calculated by the azimuth integrated curves. As shown in Fig. 3, the initial lamellae structure has a high orientation arrangement. After the first stretching, the lamellae's orientation degree slightly decreases from 0.9 to 0.79 after 100% strain and then shows no change in the later cyclic tensile. It is obvious that the regularity of lamellae arrangement is not affected by the later stretching. Among them, the first 20% strain during the first tensile shows the most obvious effect on the lamellae orientation, which may be related to the interface separation in the low tie chain density distribution zone. The interface separation and the break of the tie chain induce the initial intercrystallite crazing and change the lamellae arrangement slightly. This result proves that the lamellae are parallel separated rather than shear-deformed during stretching. The crazing mechanism of hard elastic PP film is intercrystallite crazing but not classical crazing, since no crystalline destroy occurs during stretching. On the other hand, this result also confirms that "the shearing model" and "bending model" are not suitable to describe the elasticity deformation process, since these models suggest that the orientation degree of lamellae would have an obvious change during the cyclic test.

From above SAXS patterns, the lamellae signal becomes

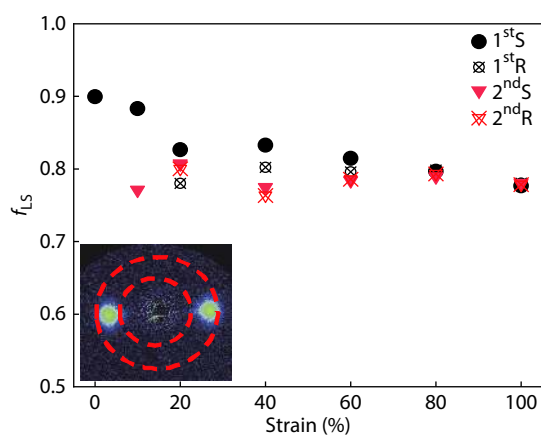


Fig. 3 The orientation degrees of lamellae during two-times cyclic stretching.

stronger and moves towards the beamstop during stretching. The integrated curves and the change of lamellae long period during cyclic stretching are followed and shown in Fig. 4. In the cyclic tensile process, the long period and its intensity are periodically increased and decreased. For the unstretched film, the intensity of lamellae is related to the density difference between the crystalline region (ρ_c) and amorphous region (ρ_{am}), i.e. $I_0 \propto (\rho_c - \rho_{am})^2$. After stretching, the crystalline degrees are nearly unchanged (shown in the electronic supplementary information, ESI). So, the increase of long period mainly occurs in the amorphous region since the crystalline region modulus is much larger than that of amorphous region. The enhancement of long period can be treated as an increase of amorphous phase thickness. The lamellae signal intensity is related to the density reduction of extended amorphous region. During stretching, the density change in the amorphous region can be described as $\rho_{am}/(1 + \epsilon_{am})$ and $\epsilon_{am} \approx \epsilon_L = \frac{L - L_0}{d_{am}}$, where ϵ_{am} is the strain in the amorphous region, L and L_0 are the lamellae long period in the tensile process and initial length, and d_{am} is the initial thickness of amorphous region. So, the intensity of lamellae gradually increases with the strain enlargement. In the recovery process, the density difference between the two phases decreases, accompanying with the shrinkage of amorphous chains, and the lamellae scattering signal becomes weak. We notice that the long period cannot totally return to the initial length due to the hysteresis of chain motion in the amorphous phase. The enhancement of long period in the first stretching process is slightly larger than that in the second step. A part of molecule chains are stretched to be broken accompanying with the formation of intercrystallite crazing. The elongation of intercrystallite crazing becomes easier in the later step. Based on these results, we can further speculate that the extension and contraction in amorphous chains decide the hard elastic material's elastic deformation.

Since the transverse size of samples barely changes during deformation and the thickness of the sample is only one-thousandth of the width, we can approximately assume that when the macroscopic strain (ϵ_{macro}) is 100%, the volume growth is also 100%. But when ϵ_{macro} is 100%, the long period is about 30 nm and the increasing rate of long period (ϵ_L) is only 60%, as shown in Fig. 5(a). The approximate 40% volume increase is due to the number of nano-cavities in the intercrystallite crazing. These results are similar to that of the semi-crystalline polymer stretched to large strain in active liquid medium. Hence, we use ϵ_L and the difference between macroscopic strain and long period's strain (ϵ_{am}) to represent the material volume expansion and the cavity volume percent. In the stretching process, ϵ_L is nearly linearly increased with the strain, but ϵ_{am} starts to increase after the strain is larger than 20%. This means that the intercrystallite crazing is formed at first, and the nano-cavities are fast formed in the intercrystallite crazing until the strain is larger than 20%. This strain is just the same as the point that weak scattering signals appear in the meridional direction, meaning that these weak signals are related to the nano-cavities formation. With the strain increase, the total cavity volume also shows linear increase. In the recovery stage, the nano-cavities in crazing shrink with

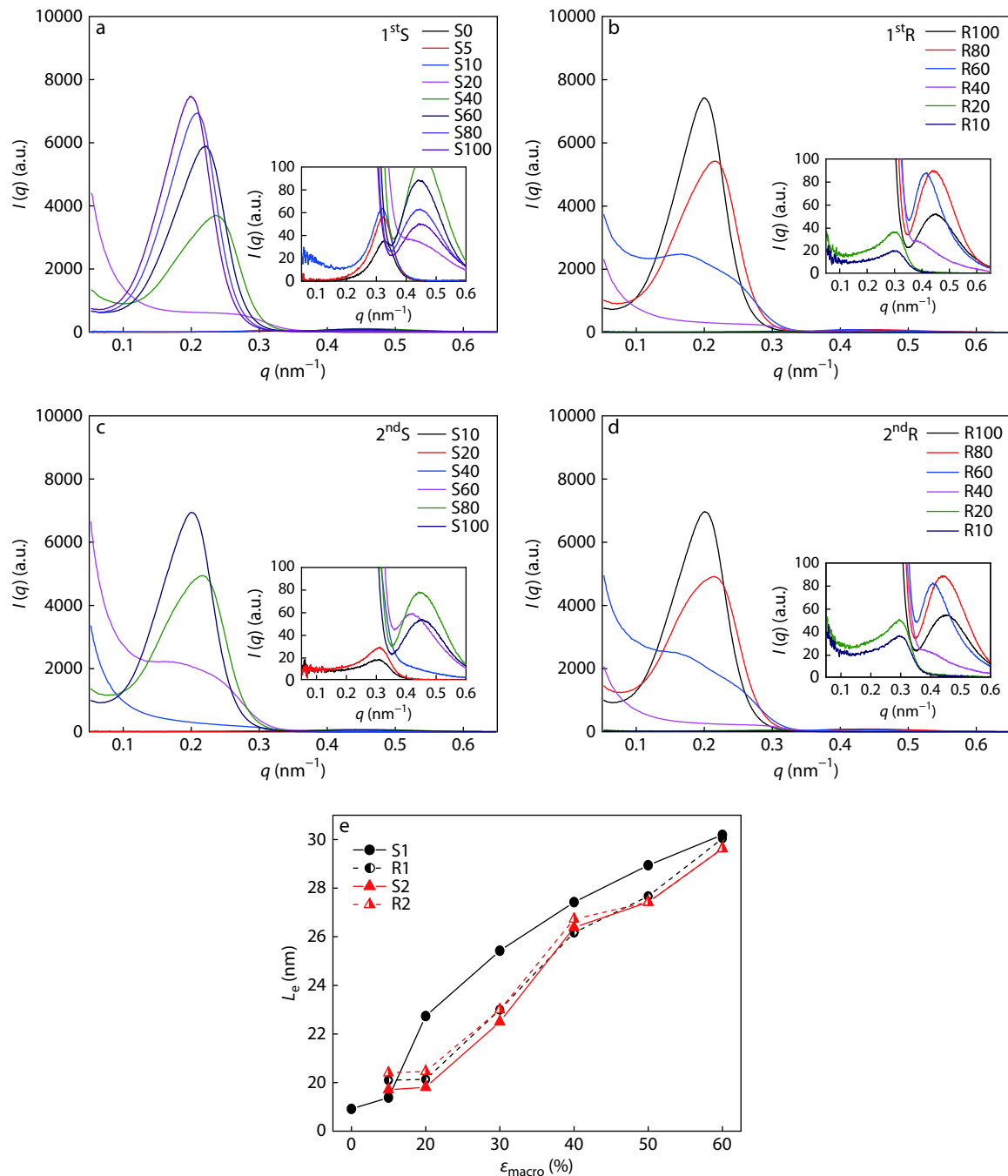


Fig. 4 The scattering intensity curves along meridional direction in two cyclic tensile (a–d) and L_e versus the macroscopic strain in two cyclic stretching (e).

molecular chain retraction. These extended amorphous chains shrink fast, which makes ϵ_{am} almost reversibly recoverable. However, a significant hysteresis occurs when the strain is reduced to 60%, as shown in Fig. 5(b). This hysteresis phenomenon is mainly due to more amorphous chains, which are stretched to break when the strain is larger than the secondary yield point. In the second cycle (Fig. 5c), ϵ_L and ϵ_{am} give the same change as the first recovery process. It is further confirmed that the formation and disappearance of nano-cavities in the intercrystallite crazing can occur reversibly during

stretching and recovery.

From the SAXS patterns, we notice that the increase of intercrystallite crazing is accompanied by the appearance of nano-cavities. The detailed evaluation of cavity structure in cyclic stretching is followed by integrating the scattering signal along the equatorial direction, as shown in Fig. 6. In the first stretching process, the scattering signal obviously increases after stretching to 10% and keeps constant after 60% strain. This region is just the strain-hardening region. Apparently, the strain-hardening is accompanied by the nano-cavit-

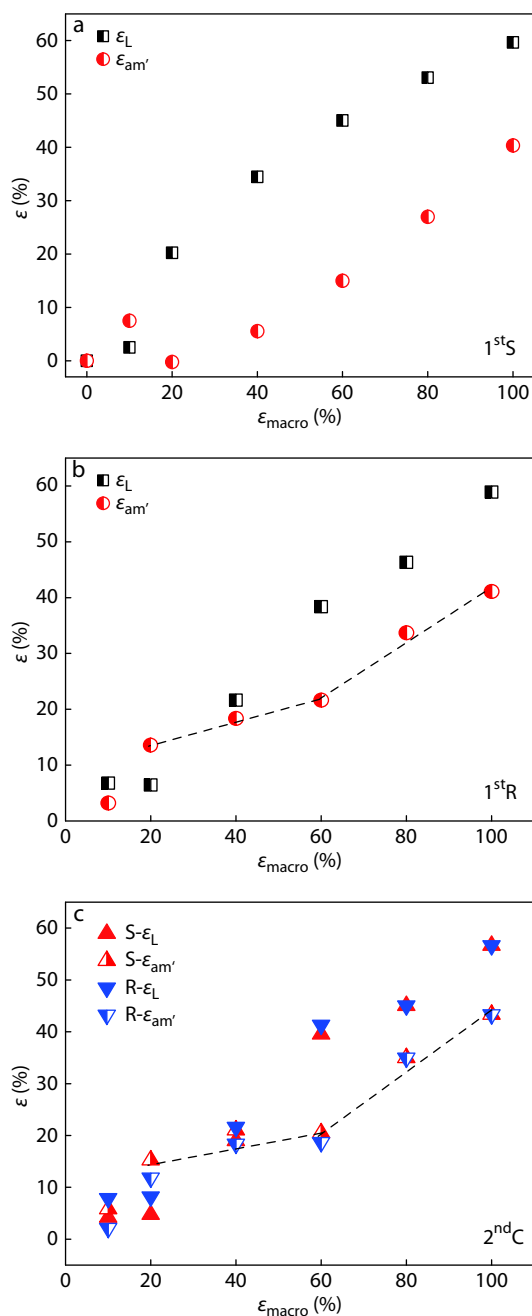


Fig. 5 ε_L and $\varepsilon_{am'}$ change in the first stretching (a), in the first recovery (b), and in the second cyclic tensile (c).

ies formation. The size and number of nano-cavity in inter-crystallite crazing are fast enhanced with amorphous region extended. After the strain is larger than the secondary yield point, the cavity's scattering signal intensity shows nearly no change. This is mainly because the nano-cavity in the inter-crystallite crazing is not a through-hole. Although the volume of the nano-cavities formed by stretching increases, the density difference between the nano-cavities and the surrounding extended amorphous regions remains basically unchanged, and the intensity of the scattered signal hardly changes. While in the recovery process, the intensity keeps constant

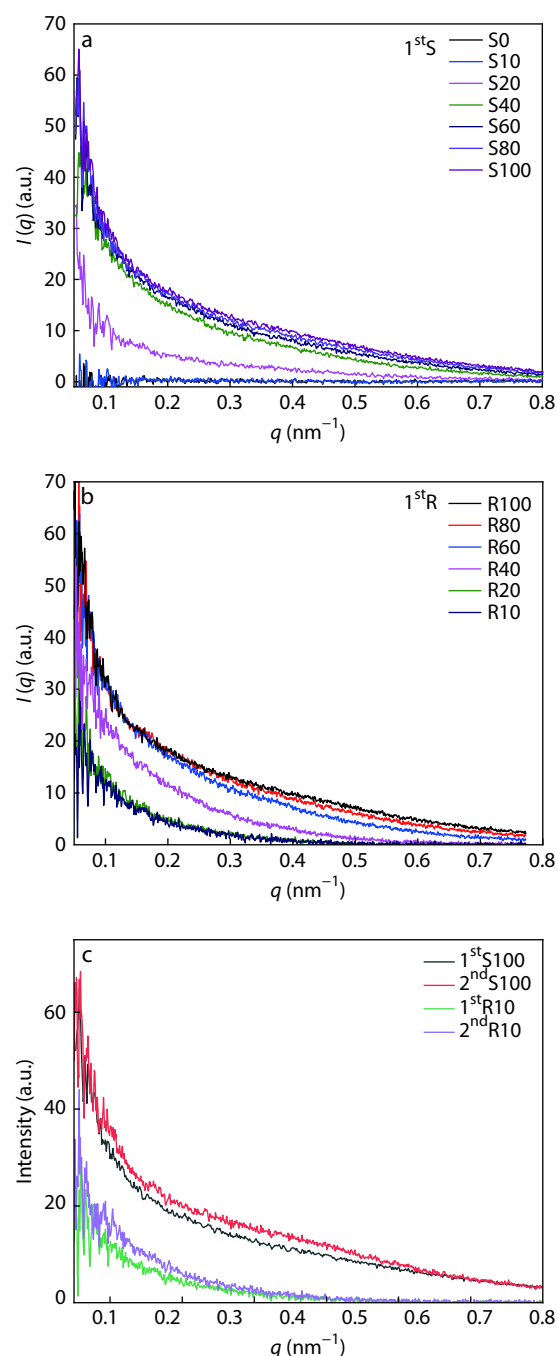


Fig. 6 The scattering intensity curves along equatorial direction in the first stretching (a) and recovery (b); the scattering intensity curves along equatorial direction at the S100 and R10 in twice cyclic stretching (c).

from 100% to 60% and shows a decrease from 60% to 10%, indicating that the nano-cavities may shrink. But the final intensity is much larger than that of tensile 10%, meaning that a few nano-cavities cannot close in the recovery. With the cycle number increasing, the scattering intensity curves keep nearly constant. This reversible change also indicates that the surface energy of nano-cavity contributes significantly to the recovery of hard elasticity.

The changes of surface energy and surface area of the nano-cavities in the recovery process are followed, as shown in Fig. 7. Through the semi-quantitative estimation of the contribution of surface energy (F_s) to retractive force, the relationship between surface energy and elastic recovery can be built.^[32,40] The surface area of nano-cavities is calculated by the SAXS scattering curve along the equatorial direction based on the Yefimov's method.^[33,41] The detailed calculation method has been given in our previous work.^[34] In the recovery process, the changes of F_s and the surface area are similar. The unstable nano-cavities with high surface area would fast shrink firstly, indicating the surface energy transfers to kinetic energy in the initial recovery step. When the recovery strain is smaller than the secondary yield point, F_s is constant, which means that the elastic resilience driven by energy elasticity becomes very limited. Although the surface area becomes very small, it does not become zero. Some nano-cavities formed by the molecular chains broken in the intercrystallite crazing region remain in the recovery process. This irreversible damage also causes the elastic recovery value not to be 100%, and the elastic recovery value decreases with the increasing time of stretching.

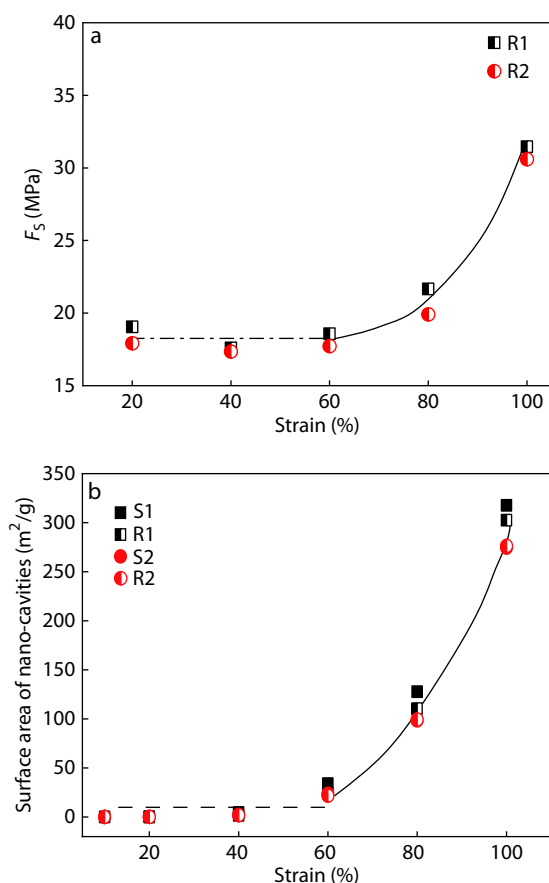


Fig. 7 The change of F_s (a) and surface area (b) of nano-cavities in twice recovery processes.

In addition to the contribution of surface energy induced by the nano-cavities inside the intercrystallite crazing, the entropy elasticity induced by the contraction of the molecular chain also shows a great influence. Hence, we track the ori-

entation of the chain segment during cyclic stretching by *in situ* FTIR. The characteristic bands at 998 and 2723 cm^{-1} are related to the crystalline and amorphous regions, respectively.^[31,42] Fig. 8 gives the crystalline and amorphous regions' orientation degree evolution in the two cyclic tests. In the first tensile process, the orientation of the molecular chains in the crystalline region shows a little decrease. However, in the amorphous region, the orientation of the molecular chains increase from 0.47 at 0% strain and reaches 0.63 at 70% strain. Obviously, when the long tie chains running through several lamellae break, the amorphous region can be extended freely along the stretching direction. In the secondary yield region, the increase of orientation of the amorphous chain lags, which may be related to the constrained stretching of the amorphous chain in the lamellae clusters. In the recovery process, the crystalline orientation is restored to the initial value due to the elastic recovery of the lamellae, while the amorphous region orientation decreases due to the reversible retraction of the amorphous chain. In the second cycle, the change of orientation degree is similar as above. The results further indicate that the entropy change caused by the reversible deformation of the amorphous chain "extension-retraction" has an important contribution to the elastic recovery of hard elastic materials.

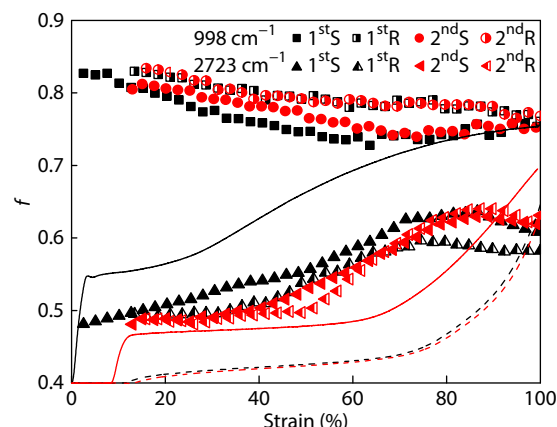


Fig. 8 The orientation degree obtained from 998 or 2723 cm^{-1} band as function of strain in the first and second cyclic tests.

From the above results, for elastic recovery, both entropy elasticity (the relaxation process of extended molecular chains in amorphous region) and energy elasticity (the surface energy of nano-cavities in the intercrystallite crazing) show some contributions. Then, their contributions to hard elastic properties are distinguished. To confirm the effect of chain relaxation on the elasticity recovery, the elastic recovery value of the hard elastic film under the condition of 100% strain was tested at different relaxation time, as shown in Fig. 9. The solid line represents the force relaxation curve and the points are the elastic recovery value at different relaxation time. This result shows that the elastic recovery reduces slightly with the relaxation time elongation. When the film is fixed at 100% strain, the relaxation process is mainly due to the relaxation of crystalline region and a part of amorphous chains retraction induces the nano-cavities shrinkage.^[2,3] Ob-

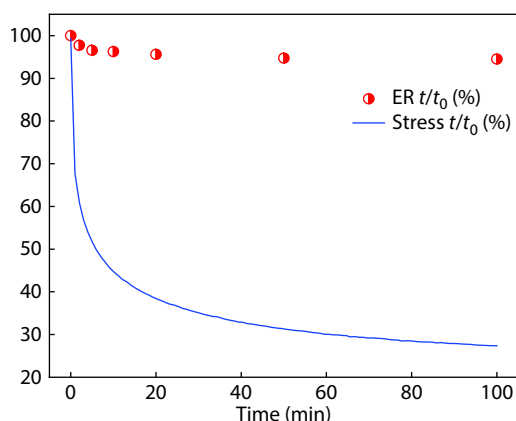


Fig. 9 The stress relaxation curves and the elastic recovery ratio at different relaxation time.

viously, the relaxation of the chain segment does not affect the elastic recovery of hard elastic materials.

To investigate the moving sequential order of the amorphous and the crystalline phase in the recovery process, the FTIR 2D correlation spectroscopy method is used. The 2D correlation spectroscopy has been demonstrated to be a very powerful and versatile tool for probing subtle spectral changes induced by an external physical variable, which can be used to reveal the sequential order of different bands.^[43,44] The 2D correlation analysis is performed on the difference spectra of the deformed specimens, to get the synchronous 2D correlation spectrum and asynchronous 2D correlation spectrum (shown in Fig. S2 in ESI). According to Noda's rules, the sequential order of different bands can be determined.^[44,45] Table 1 shows the sequential order of 998 and 1153 cm^{-1} in the recovery process. The characteristic bands at 1167, 841, 998, and 972 cm^{-1} are sensitive to crystalline phase, corresponding to helical structures with 14, 12, 10, and 5 monomers units in helical sequences, respectively.^[43] The

characteristic band at 1153 cm^{-1} is related to the amorphous region.^[42] At the strain 100%–60% of recovery process, the movement of crystalline phase occurs prior to amorphous phase, indicating that the nano-cavities shrinkage drives the lamellae cluster retraction at first, whereas in the later stage of all recovery process, the chain shrinkage of amorphous region plays a leading role in elastic recovery. It can be considered that the energy elasticity contributes more to the elastic recovery in the secondary yield zone, while the entropy elasticity in the amorphous zone contributes more to the elastic recovery in the strain-hardening zone.

Table 1 The sequential order of characteristic bands in recovery process.

Sequential order at strain 100%–60% (cm^{-1})	Sequential order at strain 60%–15% (cm^{-1})
1 st R 998 $\approx$ 972 > 1167 > 841 > 1153	1153 > 1167 > 841 > 972 > 998
2 nd R 998 $\approx$ 972 > 841 > 1167 > 1153	1153 > 1167 > 841 > 998 $\approx$ 972

Then we can roughly describe the structural evolution during stretching and recovery, as shown in Fig. 10. In the tensile process, the low tie chain density zone between the lamellae crystals and the adjacent amorphous regions is broken at first. The initial intercrystallite crazing is formed in the first yield plateau zone. Then in the strain-hardening process, the elongation of amorphous region increases with the sample stretching, resulting in the long period increasing. At the same time, the nano-cavities appear in the intercrystallite crazing. Some nano-cavities are formed by broken molecular chains. The parallel lamellae clusters are further separated in the secondary yield zone. The lamellae long period and the volume of nano-cavities continue to expand. In the recovery process, the unstable nano-cavities with high surface area shrink at first and the surface energy transfers to kinetic energy. Then the amorphous region continues to shrink, and this entropy reduction allows the rebound to continue. The interface separation during the intercrystallite crazing formation is irreversible, leading to the destruction of the continu-

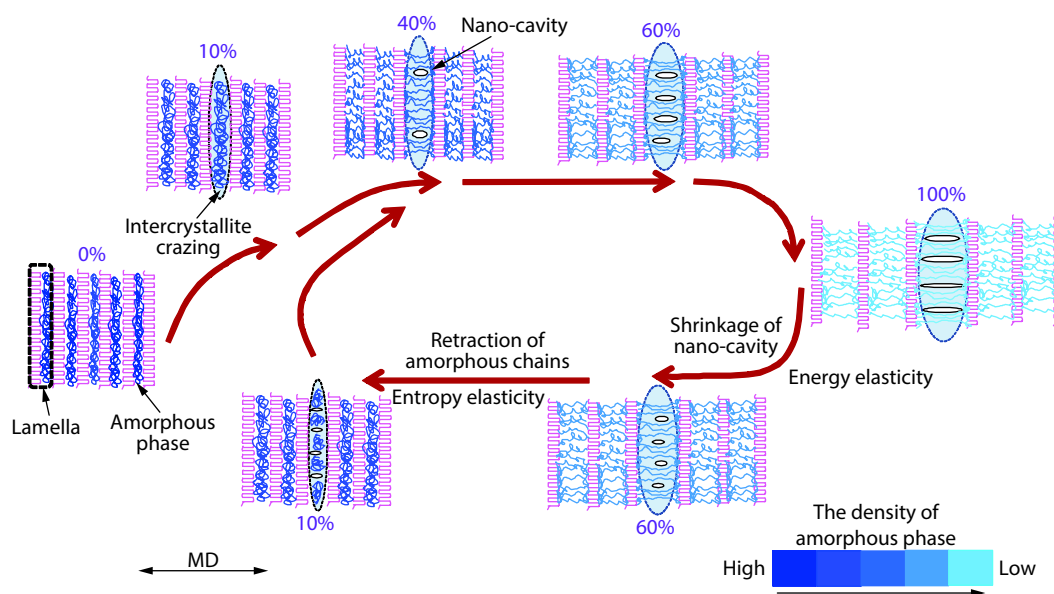


Fig. 10 The schematic diagram of hard elastic PP film structure evolution in stretching and recovery process under room temperature.

ity of the hard elastic material, but it does not affect the performance of hard elasticity. In general, the lamellae skeleton is hardly broken in tensile deformation. The energy elasticity provided by surface tension firstly drives the shrinkage of material, and then the entropy elasticity related to amorphous chain relaxation plays a leading role in elastic recovery when the strain is smaller than the secondary yield point.

CONCLUSIONS

In this work, the structure deformation of PP hard elastic film in twice cyclic tensile experiment is followed by *in situ* SAXS and FTIR, and the elasticity source is discussed. The *in situ* SAXS results show that the lamellae crystals are separated in parallel and recover in periodically tensile process. In the first stretching, some intercrystallite crazing is formed. The long period of lamellae crystals is linearly increased, and the nano-cavities in the intercrystallite crazing appear in large numbers when the strain is larger than 20%. The intercrystallite crazing cannot retract totally due to the molecular chains broken and amorphous chain's movement lagging. The results of SAXS/FTIR show that the deformation mainly occurs within the amorphous region during stretching, whereas the crystalline regions are seldom deformed. In the cyclic stretching process, the chain's movement in amorphous region is reversible. The extension and shrinkage of amorphous region act an important role in elasticity deformation. In the recovery process, the energy and entropy elasticity co-act. Before the secondary yield point, the unstable nano-cavities in the intercrystallite crazing fast shrink by the effect of surface energy. At this time, the energy elasticity provided by surface tension actuates the material shrinkage. And then, the entropy elasticity induced by amorphous chain retraction plays the main role. At this point, the hard elastic film begins to recover slowly. All these structures and energy evolution appear periodically in the cyclic tensile process. This result gives a clearer recognition about the source of hard elastic property. The contribution of energy and entropic elasticity cannot be separated absolutely. The retraction of the amorphous chains is the main factor for the periodic elastic recovery of hard elastic materials.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2432-8>.

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