Transparency of Temperature-responsive Shape-memory Gels Tuned by a Competition between Crystallization and Glass Transition

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Electronic Supplementary Information

Abstract Transparency is often an important property in the practical applications of temperature-responsive shape-memory gels. We investigated the mechanism of significant transparency improvement upon a change in two copolymer gels with their molar ratios between stearyl acrylate and N,N-dimethylacrylamide from 1:1 to 0.75:1. By means of Flash DSC measurement, we made the thermal analysis characterization of crystallization and glass transition in two copolymer gels and compared the results to the parallel experiments of corresponding homopolymers. The results showed that the slightly lower content of stearyl acrylate sequences suppresses crystallization in their side chains due to the chemical confinement of comonomers on copolymer crystallization; meanwhile it shifts up the glass transition temperature of the backbone N,N-dimethylacrylamide sequences. Eventually on cooling, crystallization gives its priority position to glass transition in copolymer gels, resulting in a higher transparency of the gel without losing the shape-memory performance. To confirm the chemical confinement, we further compared the isothermal crystallization kinetics of stearyl acrylate side chains in the copolymer gel to that of their homopolymer. Our observations facilitate the rational design of the temperature-responsive shape-memory gels for the transparency property.

Keywords Gels; Shape memory; Copolymer; Crystallization; Glass transition

Citation: Wang, Y. H.; Gong, J.; Hu, W. B. Transparency of temperature-responsive shape-memory gels tuned by a competition between crystallization and glass transition. Chinese J. Polym. Sci. 2020, 38, 1374–1381.

INTRODUCTION

Shape-memory polymers have attracted enormous attention for their shape recovery property, that is, after being deformed and fixed into a temporary shape, they can recover the original shape by stimuli-responsiveness. Temperature-responsive shape-memory gels (TSMGs) are shape-memory materials triggered by thermal stimulus, displaying the thermally induced shape memory that has been designed for intelligent materials, optical devices, and biomedical tools. In many of the potential applications, the transparency is often an important property for TSMGs. Recently, as the triggering temperature nearby the body temperature, novel TSMGs were prepared by bulk copolymerization of N,N-dimethylacrylamide (DMAA), stearyl acrylate (SA), and the crosslinker N,N′-methylenbisacrylamide (MBAA). The freeze of the stretching state on cooling and the retraction on heating of these TSMGs are usually triggered by fast crystallization and melting of the side chains of n-alkyl acrylate, respectively. Although crystallization of side-groups limits the crystalline domains in the nanometer scales, the aggregation of nanometer crystalline domains can raise the sizes of crystalline-rich and amorphous-rich regions up to the wavelengths of visible lights (few hundred nanometers) and thus ruins the transparency of TSMGs, as observed for example in bottlebrush atactic poly(1-octadecene). However, as demonstrated in Fig. 1, the transparency in the frozen stretched states of the above copolymer gels has been found to be significantly improved by a slight change in their chemical compositions (their molar ratios between SA and DMAA from 1:1 to 0.75:1). The content of SA holding the crystallizable side chains was slightly reduced, which seems to suppress significantly the crystallinity in the frozen stretched state with a better transparency, although the performance of shape memory still remains (see the movie in the electronic supplementary information, ESI). Therefore, it is worthy of a detailed thermal analysis characterization on their crystallization behaviours, in order to figure out the mechanism of such a significant transparency.

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Received March 28, 2020; Accepted May 11, 2020; Published online July 9, 2020

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Institute of Chemistry, Chinese Academy of Sciences
Springer-Verlag GmbH Germany, part of Springer Nature 2020

https://doi.org/10.1007/s10118-020-2456-0

Chinese J. Polym. Sci. 2020, 38, 1374–1381
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Polymer crystallization has been broadly investigated as reported in the numerous books and reviews. 

Specifically, the chemical confinement effects of comonomers on the crystallization behaviors of statistical copolymers have been recognized. 

The kinetics of polymer crystallization is the essential process in polymer processing to control the product crystallinity and the semi-crystalline morphology. Differential scanning calorimetry (DSC) is the common analytical tool to characterize kinetics of polymer thermal transitions including glass transition, crystallization, melting, but its time constant is 100 s or longer due to the current apparatus design, which limits its kinetic characterization of fast crystallization like the present case of fast side-chain crystallization of copolymer gels. Recently, the development of fast DSC measurement to systematically study crystallization, melting, and glass transition, improving the transparency in their frozen stretched states without losing the shape-memory performance.

**EXPERIMENTAL**

**Sample Preparation**

The samples of TSMGs were random copolymers synthesized by bulk copolymerization as reported. In this process, stearyl acrylate (SA), N,N-dimethylacrylamide (DMAA), N,N'-methylenebisacrylamide (MBAA), and benzophenone (BP) were mixed and stirred, separately as a crystallizable monomer with a crystallizable long side chain, a non-crystallizable hydrophilic comonomer, a crosslinker, and a UV polymerization initiator. After that, the solution was exposed to a UV lamp at 35 °C for 24 h in a mold, finally forming the polymerized TSMG sheets. In the present study, the prepared two different TSMGs with different molar ratios of SA and DMAA both showed the shape memory response to temperature. The white-to-transparent (WT) sample (SA:DMAA = 1:1) changes from white to transparent and back to white upon elevating the temperature and then lowering the temperature. The transparent-to-transparent (TT) sample (SA:DMAA = 0.75:1) remains transparent through the same processes. At the room temperature, the frozen stretched states of WT and TT are opaque and transparent, respectively, as shown in Fig. 1. For comparison, two corresponding homopolymers, i.e. poly(N,N-dimethylacrylamide) (PDMAA) and poly(stearyl acrylate) (PSA), were also prepared by bulk polymerization but without crosslinking. And for the random copolymers, the same crosslinking density was ensured by controlling the similar amount of crosslinking agent. The chemical compositions and the relative molar ratio used in this work are listed in Table 1. All the samples were dried for 24 h in a vacuum oven at 40 °C to remove water so that the thermal analysis experiments would not be disturbed by the residue of water.

| Sample | Monomer (mol) | Comonomer (mol) | Crosslinker (mol) | Initiator (mol) |
|--------|---------------|-----------------|------------------|----------------|
| WT     | 1             | 1               | 0.10             | 0.20 × 10⁻²   |
| TT     | 0.75          | 1               | 0.0875           | 0.175 × 10⁻²  |
| PSA    | 1             | –               | –                | 1 × 10⁻²      |
| PDMAA  | –             | 1               | –                | 0.1 × 10⁻²    |

**Colorimetric Measurement**

The Mettler-Toledo Flash DSC 1 apparatus equipped with UF51 chip-sensor and Huber TC-100 intracooler was employed in this work, operated in a nitrogen atmosphere with a continuous flow rate of 50 mL min⁻¹.

The new chip-sensor was conditioned and corrected according to the instrument manual prior to use. The bulk sample was cut into small pieces by employing a scalpel and a stereomicroscope, then was loaded to the sensor center by utilizing a single-hair tool. To improve the thermal contact between the sensor surface and the sample, the sample was pre-melted for several times under the scanning rate of...
1 K·s⁻¹ until the curves of heat flow rates remained unchanged. For comparison of the scanning results, the heat flow rate was normalized to the scanning rate and transformed into the apparent heat capacity by using the software Mettler-Toledo STAR® 11.00 version. Furthermore, since we evaluated the relative enthalpy changes of melting and crystallization in the same samples, the sample mass was not estimated.

In the following measurement, we performed non-isothermal crystallization experiments at various cooling and heating rates to check the crystallization behaviors. We compared the results of random copolymers to those of two homopolymers. After that, isothermal crystallization experiments were implemented at different temperatures and time to obtain the crystallization halftime and compare the isothermal crystallization kinetics between WT and the homopolymer PSA.

RESULTS AND DISCUSSION

Cooling at Various Cooling Rates from the Melt

We started with our observations of the cooling processes from the melt at various cooling rates for four samples of WT, TT, PSA, and PDMAA, followed with their heating curves under fixed high heating rates, as the temperature-time protocol illustrated in Fig. 2. To be more specific, each sample was first heated at 1000 K·s⁻¹ to a high enough temperature to erase the thermal history for 0.2 s. For WT, TT, PSA, and PDMAA, the high temperature for erasing their thermal history was 110, 200, 140, and 250 °C, respectively. After that, the melts were cooled down to −100 °C at various cooling rates from −10 K·s⁻¹ to −4000 K·s⁻¹ to investigate the possible melt-crystallization behaviors. And then, each sample was reheated back to observe the possible melting behaviors at the fixed heating rate of 1000 K·s⁻¹. The cooling curves and corresponding subsequent heating curves of all samples indicated by apparent heat capacity are illustrated in Figs. 3 and 4, respectively.

![Fig. 2](https://doi.org/10.1007/s10118-020-2456-0)

![Fig. 3](https://doi.org/10.1007/s10118-020-2456-0)

**Fig. 2** Temperature-time profile for cooling at various rates followed with heating at the constant high rates to observe crystallization and melting.

**Fig. 3** Cooling curves of apparent heat capacity as a function of temperature, obtained on cooling at different cooling rates as labeled near the curves for (a) WT, (b) TT, (c) PSA, and (d) PDMAA. The red dashed lines are guiding the eyes for the observed transitions.
Fig. 4  Heating curves of apparent heat capacity as a function of temperature, obtained on heating at a constant heating rate of 1000 K·s−1 after cooling at different cooling rates as labeled near the curves for (a) WT, (b) TT, (c) PSA, and (d) PDMAA. The blue dashed lines are guiding the eyes for the observed transitions.

Fig. 3 summarizes the cooling curves of four samples obtained at various cooling rates as labeled. As for the random copolymer WT, one can see from Fig. 3(a) that the crystallization peaks around 30 °C shift to lower temperatures and meanwhile become much broader with increasing cooling rates. Even the fastest cooling with −4000 K·s−1 could not completely hinder the crystallization. Crystallization here is apparently making the shape-memory performance of WT gel. In contrast, the random copolymer TT in Fig. 3(b) exhibits no exothermic crystallization peak but two glass transition steps separately around 45 and −30 °C. One can learn that the glass transition around 45 °C is responsible for the maintenance of shape-memory performance of TT gel. In comparison to the homopolymer PSA shown in Fig. 3(c), the crystallization peak around 40 °C for PSA shifts down to 30 °C for WT at the slowest cooling rates, reflecting the chemical confinement of SA-sequence crystallization in the copolymer sample. Meanwhile, in comparison to the homopolymer PDMAA shown in Fig. 3(d), the significant glass transition occurs at much higher temperature around 120 °C owing to the high rigidity of DMAA sequences. In copolymers, due to the flexible comonomer SA, the glass transition temperature of DMAA sequences will be significantly shifted down from 120 °C in homopolymer to 45 °C in random copolymer at the cooling rate −30 K·s−1. In this sense, one can assign the high glass transition temperature of the copolymer TT around 45 °C to DMAA sequences, and the low glass transition temperature around −30 °C to SA sequences due to the suppression of SA crystallization. Indeed, the glass transition temperature of long alkane side-groups has been found at −30 °C.[26] Therefore, there exists a kinetic competition between crystallization of SA sequences and glass transition of DMAA sequences around the body temperature. Slight decrease of the molar ratio between SA to DMAA sequences from 1:1 to 0.75:1 will shift down the crystallization temperature and meanwhile shifts up the glass transition temperature as shown in our present experiments. Eventually on cooling, crystallization gives its priority position to glass transition. More samples holding copolymer compositions between these two will exhibit the more detailed continuity of switching from crystallization to glass transition on cooling. Crystallization in WT gel reduces the transparency in its frozen stretched state, while glass transition in TT gel can keep the transparency of the molten gel in its frozen stretched state without sacrifice of the shape-memory performance. Our observations here explain the results demonstrated in Fig. 1.

The melting in the subsequent heating is another side of shape-memory performance of the gels. Fig. 4 summarizes the subsequent heating curves of the above four samples at fixed high heating rates after cooled at different cooling rates as labeled. For WT gel in Fig. 4(a), the melting temperature is around 40 °C and extends to 60 °C, good for a hot water treat-
ment of TSMGs. Again, the melting peak demonstrates that even the cooling rate as high as $-4000 \text{ K s}^{-1}$ could not suppress the crystallization on cooling. As for TT gel in Fig. 4(b), the glass transition temperature around 50 °C is also good for the shape-memory performance of TSMGs nearby the body temperature. In comparison, the homopolymer PSA exhibits the melting temperature around 40 °C but extends to 80 °C, higher than that of the random copolymer WT. The extension of melting peaks could be attributed to the melting-recrystallization behaviors, which will be ruled out by the variation of heating rates shown below. Here, the extents of broadening of melting peaks exhibit insensitivity to the cooling rates, as shown in Fig. 4(c). The homopolymer PDMAA shows the glass transition around 165 °C, much higher than 120 °C for the glass transition in the cooling processes, probably due to the high heating rate.

**Heating at Various Heating Rates from the Fast-frozen State**

Although the fast cooling could not suppress crystallization in WT gel and PSA, the crystals may perform significant annealing behavior in the subsequent heating process. Next, we observe the heating process at various heating rates after the fast cooling process. The temperature-time protocol is illustrated in Fig. 5. After erasing the thermal history, the melt was cooled down to $-100 ^\circ \text{C}$ at the cooling rate of $-4000 \text{ K s}^{-1}$ for WT, TT, PSA, and PDMAA, followed with various heating rates from 10 K s$^{-1}$ to 10000 K s$^{-1}$. Fig. 6 summarizes the heating curves of apparent heat capacity at various heating rates as labeled for four samples.

Fig. 6(a) shows broad melting peaks of WT gel from 10 °C to 45 °C at the heating rate 30 K s$^{-1}$ and the stable peak temperatures below 1000 K s$^{-1}$, indicating significant annealing behaviors upon slow heating. In contrast, no endothermic peak shows up in Fig. 6(b) for TT gel except for two glass transition steps consistent with the cooling processes with

![Fig. 5](https://doi.org/10.1007/s10118-020-2456-0)

**Fig. 5** Temperature-time profile for crystallization of the samples in the heating process with various heating rates after fast cooling from the melt.

**Fig. 6** Heating curves of apparent heat capacity as a function of temperature, obtained from the heating processes at different heating rates as labeled near the curves, after fast cooling at $-4000 \text{ K s}^{-1}$ from the melt for (a) WT, (b) TT, (c) PSA, and (d) PDMAA. The blue dashed lines are guiding the eyes for the observed transitions.
various cooling rates. The homopolymer PSA shown in Fig. 6(c) exhibits double melting peaks with the high-temperature peaks more sensitive to the heating rates than the low-temperature peaks, ruling out the melting-recrystallization behavior with which the high-temperature melting peak would be less sensitive to the heating rates and become higher at slower heating. Therefore, the double peaks could be attributed to two crystallites forming at the same temperatures on cooling but holding with intrinsically different stabilities on heating. We leave this behavior here for future investigation.

The homopolymer PDMAA shows only the glass transition at the high temperature region of Fig. 6(d), and shifts toward 160 °C at high heating rates, consistent with the results shown in Fig. 4(d).

Comparing the Isothermal Crystallization Kinetics between WT and PSA

Since there exists a kinetic competition between crystallization and glass transition on cooling, the knowledge about isothermal crystallization kinetics of WT in comparison to the homopolymer PSA is helpful for our understanding on the chemical confinement in copolymer crystallization. It is also possible that when the temperature becomes low enough, the hidden glass transition may beat over the crystallization if the latter is not fast enough. To this end, we traced the melting enthalpies of the heating curve after various periods of isothermal crystallization at a specific temperature. The temperature-time protocol of isothermal crystallization is illustrated in Fig. 7. From the melt, the sample was cooled fast enough, i.e. −4000 K·s⁻¹, to a specific temperature for a certain period of isothermal crystallization, followed with an immediate fast heating at the heating rate of 200 K·s⁻¹ for a sharp melting peak.

Fig. 8 separately demonstrates the heating curves for WT and PSA at the heating rate 200 K·s⁻¹ after various periods of isothermal crystallization correspondingly at 39 and 48 °C.

**Fig. 7** Illustration of the temperature-time protocol for isothermal crystallization of WT and PSA.

**Fig. 8** Heating curves of apparent heat capacity after isothermal crystallization for various periods as labeled for (a) WT at 39 °C and (c) PSA at 48 °C. Melting enthalpy versus crystallization period curves for (b) WT at 39 °C and (d) PSA at 48 °C, obtained from the melting peaks in (a) and (c), respectively, for the estimation of the crystallization halftime.
(For the heating curves at other temperatures, please see the data file in ESI). An incubation period for the initiation of crystallization can be observed as the absence of melting peaks for both samples in the early stage of isothermal crystallization. The crystallization halftime at a certain crystallization temperature was thus estimated by the crystallization-time evaluation of the melting enthalpy, as demonstrated in Figs. 8(b) and 8(d).

Fig. 9 summarizes the obtained crystallization halftime for WT and PSA at various temperatures. One can see the significant shifting down of the crystallization temperature of the copolymer WT in comparison to the homopolymer PSA due to the chemical confinement of the non-crystallizable comonomers in WT. The curves for both WT and PSA exhibit only the high-temperature branches, similar to those of polyethylene and its copolymers with fast crystallization.[45] In WT, the glass transition of the backbone DMAA sequence was blocked by the crystallization of the side groups of SA sequences, which was expected to be shifted down below the crystallization temperature range of WT. Even as low as 30 °C, the crystallization with the halftime 0.1 s remains to occur.

**Fig. 9** Crystallization halftime of copolymer WT and homopolymer PSA as a function of the isothermal crystallization temperature.

**CONCLUSIONS**

In the present work, we employed Flash DSC measurement to investigate the thermal transition behaviors of two binary random copolymer gels in comparison with their corresponding homopolymers. We observed crystallization of WT as well as glass transition of TT in the similar temperature range on cooling, resulting in contrast transparency in their frozen states. The crystallization was assigned to the side chains of SA sequences in WT, while the glass transition was assigned to the backbones of DMAA sequences in TT. The comparisons with homopolymer PSA and PDMAA confirmed the kinetic competition between crystallization and glass transition for the shape-memory performance of TSMGs in WT and TT, respectively. We further characterized the isothermal crystallization kinetics of WT and PSA to learn the extent of chemical confinement in WT. Our observations proved the scenario of competition between crystallization and glass transition as adjusted by the copolymer compositions for the contrast of transparency in the frozen states of TSMGs. The work brings new insights into the rational design of TSMGs for their transparency property. Since the water will play the role of solvent to shift down both the glass transition temperature and the crystallization temperature, we removed the water from the gels in order to simplify the present case. The effect of water content has been scheduled in the next case of our study.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2456-0.

**ACKNOWLEDGMENTS**

This work was financially supported by the National Natural Science Foundation of China (Nos. 21973042 and 21734005), Program for Changjiang Scholars and Innovative Research Teams (No. IRT1252), CAS Interdisciplinary Innovation Team, and JSPS KAKENHI 18K05228.

**REFERENCES**

1. Lendlein, A.; Kelch, S. Shape-memory polymers. *Angew. Chem. Int. Ed.* 2002, 41, 2034–2057.
2. Behl, M.; Lendlein, A. Shape-memory polymers. *Mater. Today* 2007, 10, 20–28.
3. Liu, C.; Qin, H.; Mathers, P. T. Review of progress in shape-memory polymers. *J. Mater. Chem.* 2007, 17, 1543–1558.
4. Huang, W. M.; Ding, Z.; Wang, C. C.; Wei, J.; Zhao, Y.; Purnawali, H. Shape memory materials. *Mater. Today* 2010, 13, 54–61.
5. Xie, T. Recent advances in polymer shape memory. *Polymer* 2011, 52, 4985–5000.
6. Zhao, Q.; Qi, H. J.; Xie, T. Recent progress in shape memory polymer: new behavior, enabling materials, and mechanistic understanding. *Prog. Polym. Sci.* 2015, 49-50, 79–120.
7. Leng, J.; Lan, X.; Liu, Y.; Du, S. Shape-memory polymers and their composites: stimulus methods and applications. *Prog. Mater. Sci.* 2011, 56, 1077–1135.
8. Hu, J.; Zhu, Y.; Huang, H.; Lu, J. Recent advances in shape-memory polymers: structure, mechanism, functionality, modeling and applications. *Prog. Polym. Sci.* 2012, 37, 1720–1763.
9. Hager, M. D.; Bode, S.; Weber, C.; Schubert, U. S. Shape memory polymers: past, present and future developments. *Prog. Polym. Sci.* 2015, 49-50, 3–33.
10. Osada, Y.; Matsuda, A. Shape memory in hydrogels. *Nature* 1995, 376, 219–219.
11. Okano, T. Molecular design of temperature-responsive polymers as intelligent materials. In *Responsive gels: volume transitions II*; Dušek, K., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, 1993, pp. 179–197.
12. Osada, Y.; Gong, J. P. Soft and wet materials: polymer gels. *Adv. Mater.* 1998, 10, 827–837.
13. Sun, L.; Huang, W. M.; Ding, Z.; Zhao, Y.; Wang, C. C.; Purnawali, H.; Tang, C. Stimulus-responsive shape memory materials: a review. *Mater. Design* 2012, 33, 577–640.
14. Chatserji, S.; Kwon, I. K.; Park, K. Smart polymeric gels: redefining the limits of biomedical devices. *Prog. Polym. Sci.* 2007, 32, 1083–1122.
15. Yokoo, T.; Hidema, R.; Furukawa, H. Smart lenses developed with high-strength and shape memory gels. *E-J. Surf. Sci. Nanotech.*

https://doi.org/10.1007/s10118-020-2456-0
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16 Kabir, M. H.; Gong, J.; Watanabe, Y.; Makino, M.; Furukawa, H. Hard-to-soft transition of transparent shape memory gels and the first observation of their critical temperature studied with scanning microscopic light scattering. Mater. Lett. 2013, 108, 239–242.

17 Lendlein, A.; Langer, R. Biodegradable, elastic shape-memory polymers for potential biomedical applications. Science 2002, 296, 1673.

18 Yamano, M.; Akiaba, N.; Gong, J.; Furukawa, H. Experiments of a two-arm robot using shape memory gel. Proceedings of 2012 IEEE/SICE International Symposium on System Integration 2012, 648–653.

19 Yamano, M.; Goto, D.; Ujiie, K.; Akiaba, N.; Gong, J.; Furukawa, H.; Tadakuma, R. Experiments of a variable stiffness robot using shape memory gel. Proceedings of 2012 IEEE/SICE International Symposium on System Integration 2013, 647–652.

20 Harada, S.; Hidema, R.; Gong, J.; Furukawa, H. Intelligent button developed using smart soft and wet materials. Chem. Lett. 2012, 41, 1047–1049.

21 Kaufman, H. S.; Sacher, A.; Alfrey, T.; Fankuchen, I. Side-chain shape memory gel.

22 Lendlein, A.; Langer, R. Biodegradable, elastic shape memory polymers for potential biomedical applications. Science 2002, 296, 1673.

23 Yamano, M.; Goto, D.; Ujiie, K.; Akiaba, N.; Gong, J.; Furukawa, H.; Tadakuma, R. Experiments of a variable stiffness robot using shape memory gel. Proceedings of 2012 IEEE/SICE International Symposium on System Integration 2013, 647–652.

24 Harada, S.; Hidema, R.; Gong, J.; Furukawa, H. Intelligent button developed using smart soft and wet materials. Chem. Lett. 2012, 41, 1047–1049.

25 Matsuda, A.; Sato, J. I.; Yasunaga, H.; Osada, Y. Order-disorder transition of a hydrogel containing an α-alkyl acrylate. Macromolecules 1994, 27, 7695–7698.

26 Beiner, M.; Huth, H. Nanophase separation and hindered glass transition in side-chain polymers. Nat. Mater. 2003, 2, 595–599.

27 Pritchard, R. The transparency of crystalline polymers. Polym. Eng. Sci. 1964, 4, 66–71.

28 López-Barrón, C. R.; Tsou, A. H.; Younker, J. M.; Norman, A. I.; Schaefer, J. J.; Hagadorn, J. R.; Throckmorton, J. A. Microstructure of crystallizable α-olefin molecular bottlebrushes: isotactic and atactic poly[L-octadecene]. Macromolecules 2018, 51, 872–883.

29 Hu, W. Principles of polymer crystallization (In Chinese). Chemical Industry Press, Beijing, 2013.

30 Hu, W.; Frenkel, D. Polymer crystallization driven by anisotropic interactions. Adv. Polym. Sci. 2005, 191, 1–35.

31 Hu, W. Polymer physics: a molecular approach. Springer-Verlag: Wien, 2013.

32 Hu, W. The physics of polymer chain-folding. Phys. Rep. 2018, 747, 1–50.

33 Hu, W.; Mathot, B. V. F.; Frenkel, D. Phase transitions of bulk statistical copolymers studied by dynamic Monte Carlo simulations. Macromolecules 2003, 36, 2165–2175.

34 Hu, W.; Mathot, B. V. F.; Alamo, R. G.; Gao, H.; Chen, X. Crystallization of statistical copolymers. Adv. Polym. Sci. 2017, 276, 1–43.

35 Schick, C. Differential scanning calorimetry (DSC) of semicrystalline polymers. Anal. Bioanal. Chem. 2009, 395, 1589–1611.

36 Schawe, J. E. K.; Pogatscher, S. Material characterization by fast scanning calorimetry: practice and applications. In Fast scanning calorimetry. Schick, C.; Mathot, V., Eds., Springer International Publishing, Cham, 2016, 3–80.

37 Mathot, V.; Pyda, M.; Pijpers, T.; Vanden Poel, G.; van de Kerkhof, E.; van Herwaarden, S.; van Herwaarden, F.; Leenaers, A. The Flash DSC 1, a power compensation twin-type, chip-based fast scanning calorimeter (FSC): first findings on polymers. Thermochim. Acta 2011, 522, 36–45.

38 Van Herwaarden, S.; Iervolino, E.; Van Herwaarden, F.; Wijffels, T.; Leenaers, A.; Mathot, V. Design, performance and analysis of thermal lag of the UFS1 twin-calorimeter chip for fast scanning calorimetry using the Mettler-Toledo Flash DSC 1. Thermochim. Acta 2011, 522, 46–52.

39 Poel, G. V.; Istrate, D.; Magon, A.; Mathot, V. Preparation and calibration of the Flash DSC 1, a new, MEMS-based fast scanning calorimeter. J. Therm. Anal. Calorim. 2012, 110, 1533–1546.

40 Iervolino, E.; van Herwaarden, A. W.; van Herwaarden, F. G.; van de Kerkhof, E.; van Grinsven, P. P. W.; Leenaers, A. C. H. I.; Mathot, V. B. F.; Sarro, P. M. Temperature calibration and electrical characterization of the differential scanning calorimeter chip UFS1 for the Mettler-Toledo Flash DSC 1. Thermochim. Acta 2011, 522, 53–59.

41 Li, Z.; Zhou, D.; Hu, W. Recent progress on Flash DSC study of polymer crystallization and melting. Acta Polym. Sinica (In Chinese) 2016, 1179–1197.

42 Toda, A.; Androsch, R.; Schick, C. Insights into polymer crystallization and melting from fast scanning chip calorimetry. Polymer 2016, 91, 239−263.

43 Schick, C.; Androsch, R.; Schmelzer, J. W. P. Homogeneous crystal nucleation in polymers. J. Phys.: Condens. Matter 2017, 29, 453002.

44 He, Y.; Xie, K.; Wang, Y.; Zhou, D.; Hu, W. Characterization of polymer crystallization kinetics via fast-scanning chip-calorimetry. Acta Phys.-Chim. Sin. 2020, 36, 1905081.

45 Cavallo, D.; Gardella, L.; Alfonso, G. C.; Mileva, D.; Androsch, R. Effect of comonomer partitioning on the kinetics of mesophase formation in random copolymers of propene and higher α-olefins. Polymer 2012, 53, 4429–4437.

46 Cavallo, D.; Zhang, L.; Portale, G.; Alfonso, G. C.; Janani, H.; Alam, R. G. Unusual crystallization behavior of isotactic polypropylene and propene/1-alkene copolymers at large undercoolings. Polymer 2014, 55, 3234–3241.

47 Mileva, D.; Androsch, R. Effect of co-unit type in random propylene copolymers on the kinetics of mesophase formation and crystallization. Colloid. Polym. Sci. 2012, 290, 465–471.

48 Zhuravlev, E.; Madhavi, V.; Lustiger, A.; Androsch, R.; Schick, C. Crystallization of polyethylene at large undercooling. ACS Macro Lett. 2016, 5, 365–370.

49 Kalapati, D.; Tang, Q.; Zhang, X.; Hu, W. Comparing crystallization kinetics among two G-resin samples and PP via flash DSC measurement. J. Therm. Anal. Calorim. 2017, 128, 1859–1866.

50 Cai, J.; Luo, R.; Lv, R.; He, Y.; Zhou, D.; Hu, W. Crystallization kinetics of ethylene-co-propylene rubber/isotactic polypropylene blend investigated via chip-calorimeter measurement. Eur. Polym. J. 2017, 96, 79–86.