

Article

Photonic Contribution to the Heat Capacity Jump at T_g of Nylon-6 and Nylon-6,6 Glasses

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For the ordered part / hole pairs in nylon-6 (N6) and nylon-6,6 (N66) glasses formed by the enthalpy relaxation, the hole energy per molar photon for excited holes at T_g , $h^h = 3C_v^{\text{ph}}T_g$ ($2h^h$ for N66), was equal to the heat of fusion, h_u , of each crystal, where C_v^{ph} ($= 2.701R$) is the constant volume heat capacity for photons in holes, R is the gas constant, and the coefficient of 2.701 showed that the photon was the wave packet appeared by Fourier transformation of the frequency distribution of electric field, basing on the uncertainty principle. The finding of $h^h = h_u$ ($h^h = h_u/2$ for N66) drew that the part of four neighboring methylene sequences in two smallest crystals, corresponding to the divisions of each crystal cell, was the ordered part / hole pair containing one photon. The photonic contribution of $\Delta C_p/\Delta C_p^{\text{exp}}$ ($2\Delta C_p/\Delta C_p^{\text{exp}}$ for N66), 0.84 (0.78 for N66), showed that the end parts of crystalline methylene sequences were in glassy states, where ΔC_p ($= 44.9 \text{ J K}^{-1} \text{ mol}^{-1}$) is the heat capacity jump per molar photon and ΔC_p^{exp} is the experimental value of heat capacity jump per molar structural unit at the same glass transition.

Keywords: glass transition, heat capacity jump, photonic contribution, nylon-6, nylon-6,6



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1. Introduction

The studies of glass transition of polymers interesting for a long time because of the mysterious phenomena¹⁻⁶⁾ took the new stage by the physical finding of the photonic contribution to the glass transition, being one of the quantum phenomena.⁷⁻¹⁴⁾ The photons played the major role especially in the heat capacity jump at the glass transition. At the glass transition temperature, T_g , upon heating for polymers, the disappearance of the ordered part / hole pairs, which were formed by the enthalpy relaxation upon cooling to temperatures below T_g , was concerned with the abrupt increase of the free volume and the absorption of the glass transition enthalpy to the melt states.^{10,15)} However, because of the length distribution of ordered part / hole pairs and the reorganization after the melting of ordered parts, the free volume change was gradual seeing the temperature dependence of the free volume to the end temperature, T_i , of the glass transition.^{10,13,14)} Nevertheless, the heat capacity jump per molar photon for holes to T_i was $\Delta C_p (= 2C_v^{ph}) = 44.9 \text{ J K}^{-1} \text{ mol}^{-1}$,¹¹⁻¹⁴⁾ where $C_v^{ph} (= 2.701R)$ is the constant volume heat capacity per molar photon,¹⁶⁾ $R (= N_A k)$ is the gas constant, N_A is Avogadro number, and k is Boltzmann constant. The coefficient of 2.701 showed that the substance of a photon in the ordered part / hole pairs was the wave packet appeared by Fourier transformation of the frequency distribution of electric field,¹⁷⁾ basing on the uncertainty principle of $k\Delta T\Delta t = h/(2\pi)$, where h is Planck constant, ΔT and Δt are the respective differences of temperature (T) and time (t). Further from the excited hole energy of $h^h = 3C_v^{ph}T_g$ at T_g , corresponding to $(3/2)N_A h\nu$, the wavenumber of $1/\lambda (= \nu/c)$ was derived for several polymers,¹⁰⁻¹⁴⁾ where λ is the wavelength, ν is the frequency of light, and c is the velocity of light. At temperatures below T_g , the hole should be in a ground state. Therefore, $h^h (= C_v^{ph}T)$ is zero at $T = 0 \text{ K}$. While for isotactic polystyrene (iPS) and isotactic polypropylene (iPP) having $T_g = 360 \text{ K}$ and 270 K , respectively, the relation of $h^h = h_0^h - 3C_v^{ph}(T_g - T)$ with $h_0^h = C_v^{ph}T_g$ was shown as the generation formula of the ordered parts with the core free volume of helices in the helix-coil transition occurring upon heating from the new T_g of 240 K and

180 K for the respective glasses free from ordered part / hole pairs, which are led from the above formula at $h^h = 0$, being twice the quantum regular temperature interval of 120 K for iPS and 90 K for iPP, respectively. $\Delta C_p (= 3C_v^{ph})$ at new T_g was $67.4 \text{ J K}^{-1} \text{ mol}^{-1}$ for both polymers. In this context, the corresponding temperatures of interval, 120 K and 90 K, are to be T_g for skeletal and ideal glasses^{5,18,19)}. For poly(ethylene terephthalate) (PET) with $T_g = 342 \text{ K}$, the ordered part / hole pairs were mesophase crystals. Further the excited hole energy at T_g was equal to the heat of fusion, but the photonic contribution described in Section 4 was 0.6, because of the glassy disorder of the ethylene glycol parts in the crystals.¹⁴⁾

Nylon-6 (N6) and nylon-6,6 (N66) are polymers with T_g . However the substance of ordered part / hole pairs as described above has not been cleared yet. Recently also for these polymers, it was found that the excited hole energy of the ordered part / hole pairs at T_g was equal to the heat of fusion.²⁰⁾ So first, as the ordered part / hole pairs disappearing at T_g , two smallest crystals with the different structures corresponding to the divisions of each crystal cell were shown (see **Figs.2** and **3**).

2. Photon in Ordered Part / Hole Pairs

Table 1 shows the values of T_g , T_m^0 , h^h , h_u , h^h/h_u , and $2h^h/h_u$ for N6 and N66. The hole energy of $h^h (= 3C_v^{ph}T_g) = 21.1 \text{ kJ mol}^{-1}$ at $T_g = 313 \text{ K}$ ⁵⁾ for N6 almost agreed with $h_u = 21.3 \text{ kJ mol}^{-1}$ of the heat of fusion at the equilibrium melting temperature, T_m^0 .²¹⁾ Further also for N66, concerning with two photons per a structural unit, the hole energy of $2h^h = 43.6 \text{ kJ mol}^{-1}$ at $T_g = 323 \text{ K}$ ⁵⁾ almost agreed with $h_u = 43.1 \text{ kJ mol}^{-1}$ at T_m^0 .²¹⁾ Thus, the ordered part / hole pairs exciting at T_g should be the smallest crystals with $h^h = h_u$ for N6 and $h^h = (1/2)h_u$ for N66. But the cohesive energy of amide residues is not contained in h_u , because the hydrogen bonds between amide residues should be kept after melting. Therefore the part of four neighboring methylene sequences in the smallest crystals was assumed as the ordered part / hole pair, containing one photon. This meant that the molar structural unit (mol) is the same as molar photon (mol*) for N6 and $2 \times \text{mol}^*$ for N66.

Table 1 The values of T_g , T_m^0 , h^h , h_u , h^h/h_u , and $2h^h/h_u$ for N6 and N66.

Polym.	T_g ⁵⁾ K	T_m^0 ²¹⁾ K	h^h kJ mol^{-1} *1	h_u ²¹⁾ kJ mol^{-1}	h^h/h_u	$2h^h/h_u$
N6	313	498 (501)	21.1	21.3	0.99	----
N66	323	540 (542) 542 ²²⁾	21.8	43.1 43.4 ^{*2)}	----	1.01

*1: molar photon. *2: by Clapeyron equation²²⁾. The values in () of T_m^0 are our data^{23,24)}.

Fig.1 shows the wave packet of pulse in the $E - t$ plane derived from Fourier transformation of the frequency (ν) distribution of electric field (E)¹⁷ for an orthorhombic crystal model. In the steady excitation at T_g , the photon with the energy of $h\nu$ ($= 2C_v^{\text{ph}}T_g/N_A$) is emitted along the x axis continuously.

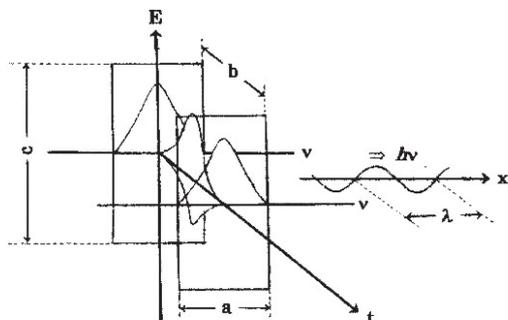


Fig.1 The wave packet of pulse with the up-and-down peaks in the t direction. a , b , and c (chain axis) are the cell length.

From the condition of limit pulse of $\Delta\nu\Delta t = 0.441$, the pulse energy, ΔU ($= h\Delta\nu$), is given as¹⁷:

$$\Delta U = 0.441h/\Delta t = 2.77h/(2\pi\Delta t) \quad (1)$$

where in **Fig.1**, $\Delta\nu$ and Δt are the full width at half maximum of the ν distribution of electric field and that of a pulse in t axis, respectively. While, approximating ΔU by the hole energy change, Δh^h ($= C_v^{\text{ph}}\Delta T/N_A$), yields the uncertainty principle in ΔT and Δt :

$$\Delta T\Delta t = 1.026h/(2\pi k) \approx h/(2\pi k) \quad (2)$$

Fig.2 shows the cell structures of $a - c$ plane in the α form crystal of monoclinic and two smallest crystals corresponding to the divisions of a crystal for N6.

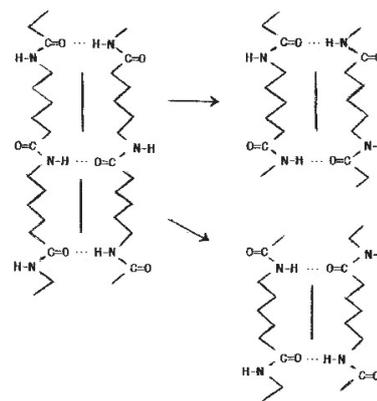


Fig.2 The cell structures of $a - c$ plane in the α form crystal of monoclinic and two divided smallest crystals for N6. The solid and dotted lines show the photon site and the hydrogen bond site, respectively.

Fig.3 shows the cell structures of $a - c$ plane in the α form crystal of triclinic and two divided smallest crystals for N66.

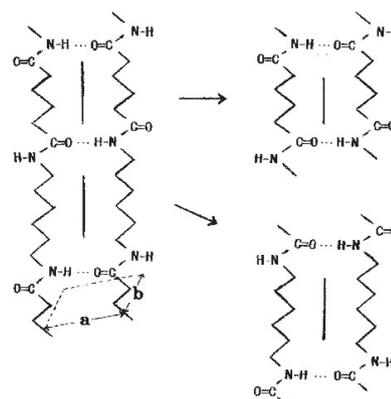


Fig.3 The cell structures of $a - c$ plane in the α form crystal of triclinic and two divided smallest crystals for N66. The solid and dotted lines show the photon site and the hydrogen bond site, respectively. a and b are the cell length of triclinic crystal.

Table 2 shows the values of T_g , h^h , λ , and $1/\lambda$ for N6 and N66. The wavenumber of $1/\lambda$ ($= \nu/c$) derived from h^h ($= 3C_v^{\text{ph}}T_g$) $= (3/2)N_A h\nu$ at T_g was found in the spectrum^{25,26}, showing the assignment of a photon.

Table 2 The values of T_g , h^h , λ , and $1/\lambda$ for N6 and N66.

Polymer	T_g ⁵⁾ K	h^h kJ mol ^{-1*}	λ μm	$1/\lambda$ cm ⁻¹	$1/\lambda$ ^{**} cm ⁻¹
N6	313	21.1	8.50	1176	1200 ²⁵⁾
N66	323	21.8	8.23	1215	1224 ²⁶⁾

*: molar photon. **: reference values being near $1/\lambda$.

3. T_g is T_m !

For crystalline polymers, Gibbs-Thomson equation in the melting temperature, T_m , and the crystal length, ζ , is known well:

$$T_m = T_m^0 \{1 - 2\sigma_e / (\zeta \mu h_u)\} \quad (3)$$

where T_m^0 is the equilibrium melting temperature, σ_e is the end surface free energy per m^2 , μ is the conversion coefficient with the unit of J/m^3 . From eq. (3), first the σ_e of crystals with $T_m = T_g$ and ζ of the usual cell length was derived. While using DSC data, the σ_e for crystals with large ζ was also derived from:^{15,27,28)}

$$\sigma_e = \mu b_0 h_u \{RT_m^2 + (H_x - h_x)(T_m^0 - T_m)\} / \{2(H_x - h_x)T_m^0\} \quad (4)$$

with $H_x = 2h_u - Q_m$

where $b_0 = 17.2 \times 10^{-10}$ m is the usual cell length of a chain axis for N6 and corresponding to c axis for N66, h_x is the enthalpy per molar structural unit for the ordered parts, T_m is DSC melting peak temperature, Q_m is the heat per molar structural unit corresponding to the area of melting peak on DSC curve.

Table 3 shows the values of $T_m (= T_g)$, T_m^0 , h_u , ζ , μ , σ_e , and σ_e^* for N6 and N66. σ_e^* is σ_e from eq. (4) under $h_x = h_u$ for crystals with large ζ , using our data of T_m^0 in Table 1^{23,24)}. The values of σ_e per one photon from eq. (3) for N6 and N66 were near those from eq. (4) for crystals with large ζ , supporting that T_g was T_m of smallest crystals as shown in **Figs.2 and 3**.

Table 3 The values of $T_m (= T_g)$, T_m^0 , h_u , ζ , μ , σ_e , and σ_e^* for N6 and N66.

Polym.	$T_m (= T_g)$ K	T_m^0 K	h_u kJ mol ⁻¹	ζ m	μ mol m ⁻³	σ_e mJ m ⁻²	σ_e^* mJ m ⁻²
N6	313	498	21.3	17.2×10^{-10}	1.09×10^4	74.2 (37.1)	47.3
N66	323	540	43.1	17.2×10^{-10}	5.49×10^3	81.7 (40.9)	37.9

The value in () is per one photon.

Table 4 The values of T_g , ΔC_p^{exp} , $\Delta C_p (= 2C_v^{\text{ph}})$, $\Delta C_p / \Delta C_p^{\text{exp}}$, and $2\Delta C_p / \Delta C_p^{\text{exp}}$ for N6 and N66.

Polym.	T_g ⁵⁾ K	$\Delta C_p^{\text{exp } 5)}$ J K ⁻¹ mol ⁻¹	ΔC_p J K ⁻¹ mol ⁻¹ *	$\Delta C_p / \Delta C_p^{\text{exp}}$	$2\Delta C_p / \Delta C_p^{\text{exp}}$
N6	313	53.7	44.9	0.84	----
N66	323	115.5	44.9	----	0.78

*: molar photon.

4. Photonic Contribution

Table 4 shows the photonic contribution of $\Delta C_p / \Delta C_p^{\text{exp}}$ ($2\Delta C_p / \Delta C_p^{\text{exp}}$ for N66), 0.84 (0.78 for N66), to the experimental value, ΔC_p^{exp} , of the heat capacity jump per molar structural unit at the glass transition, suggesting that the end parts of crystalline methylene sequences were in glassy states. From the value of $h_x/4 = 4.5$ kJ mol⁻¹ found for N6^{10,20)}, being smaller than $h_u/4 = 5.3$ kJ mol⁻¹ for crystals, $\Delta C_p / \Delta C_p^{\text{exp}}$ for N6 was formulated as:

$$\Delta C_p / \Delta C_p^{\text{exp}} = h^h / (h_x + h^g) \quad (5)$$

where h^g is the transition enthalpy per molar structural unit for glass parts. Here h^g was divided into two terms, $h^h - h_x$ and $\{(h_x + h^g) - h^h\}$, those being the energy of glass parts around the ordered part and the hole in a pair. From the approximation of $(h^h - h_x)/h_x \approx \{(h_x + h^g) - h^h\}/h^h$, the relation of $h^h / (h_x + h^g) \approx h_x / h^h$ is derived, giving $\Delta C_p / \Delta C_p^{\text{exp}}$.

Table 5 shows the values of T_g , h_x , h^g , h^h , h_x/h^h , and $(h_x/2)/h^h$ for N6 and N66. The end parts of four neighboring methylene sequences in the smallest crystals, corresponding to $(h^h - h_x)/h^h = 0.15$ for N6 and $(h^h - h_x/2)/h^h = 0.23$ for N66, should be in glassy states.

Table 5 The values of T_g , h_x , h^g , h^h , h_x/h^h , and $(h_x/2)/h^h$ for N6 and N66.

Polym.	T_g ⁵⁾ K	h_x kJ mol ⁻¹	h^g kJ mol ^{-1*}	h^h kJ mol ^{-1*}	h_x/h^h	$(h_x/2)/h^h$
N6	313	18.0	7.12	21.1	0.85	----
N66	323	33.6**	11.1	21.8	----	0.77

*: molar photon. **: estimate from $2h_u\Delta C_p/\Delta C_p^{\text{exp}}$.

5. Conclusion

For the ordered part / hole pairs in N6 and N66 glasses formed by the enthalpy relaxation, the excited hole energy per molar photon for holes at T_g , $h^h = 3C_v^{\text{ph}}T_g$ ($2h^h$ for N66), was equal to the heat of fusion, h_u , of each crystal. From $h^h = h_u$ ($h^h = h_u/2$ for N66), the part of four neighboring methylene sequences in smallest crystals was corresponded to the ordered part / hole pair, containing one photon. The coefficient of 2.701 in C_v^{ph} ($= 2.701R$) of the constant volume heat capacity for photons in holes showed that the photon was the wave packet appeared by Fourier transformation of the frequency distribution of electric field. The wavenumber of $1/\lambda$ derived from h^h at T_g , corresponding to $(3/2)N_A h\nu$, was found in the spectrum, showing the assignment of a photon. The photonic contribution of $\Delta C_p/\Delta C_p^{\text{exp}}$ ($2\Delta C_p/\Delta C_p^{\text{exp}}$ for N66), 0.84 (0.78 for N66), showed that the end parts of crystalline methylene sequences in the smallest crystals were in glassy states.

References

- 1) T. G. Fox and P. J. Flory, *J. Polym. Sci.* **13**, 315-319 (1954).
- 2) G. Natta, P. Corradini, D. Sianesi, and D. Morero, *J. Polym. Sci.* **51**, 527-539 (1961).
- 3) G. Gee, *Polymer* **7**, 177-191 (1966).
- 4) P. J. Roe and A. E. Tonelli, *Macromolecules* **12**, 878-883 (1979).
- 5) B. Wunderlich, “*Thermal Analysis of Polymeric Materials*”, Springer, (2005).
- 6) B. Wunderlich, *J. Appl. Polym. Sci.* **195**, 49-59 (2007).
- 7) N. Tanaka, *Preprints of 45th Japanese Conference on Calorimetry and Thermal Analysis* (Hachioji), p20 (2009).
- 8) N. Tanaka, *Preprints of 46th Japanese Conference on Calorimetry and Thermal Analysis* (Tsu), p27 (2010).
- 9) N. Tanaka, *Preprints of 47th Japanese Conference on Calorimetry and Thermal Analysis* (Kiryu), p64 (2011).
- 10) N. Tanaka and Y. Mastai Ed: “*Advances in Crystallization Processes*”, InTech, 163-184 (2012).
- 11) N. Tanaka, *62nd SPSJ Annual Meeting, Polymer Preprints* (CD), Kyoto, **62**, (2013).
- 12) N. Tanaka, *Preprints of 49th Japanese Conference on Calorimetry and Thermal Analysis* (Narashino), p137 (2013).
- 13) N. Tanaka, *63rd SPSJ Annual Meeting, Polymer Preprints* (CD), Nagoya, **63**, (2014).
- 14) N. Tanaka and Y. Mastai Ed: “*Advanced Topics in Crystallization*”, InTech, 157-182 (2015).
- 15) N. Tanaka, *Polymer* **49**, 5353-5356 (2008).
- 16) L. H. Hill, “*Introduction to Statistical Thermodynamics*”, Addison-Wisley, Massachusetts, p.456 (1960).
- 17) J. Takeuch, “*Fourier Transformation*”, Blue Backs B-1657, Kodansha (2012).
- 18) C. A. Angell, *Science* **267**, 1924-1935 (1995).
- 19) F. H. Stillinger, *Science* **267**, 1935-1939 (1995).
- 20) N. Tanaka, *Preprints of 51st Japanese Conference on Calorimetry and Thermal Analysis* (Hatoyama), p128 (2015).
- 21) L. Manderkern, “*Crystallization of Polymers*”, MacGraw-Hill, New York (1964).
- 22) L. Mandelkern, J. Mark Ed: “*Physical Properties of Polymers (Third Edition)*”, Cambridge Univ. Press, (2004).
- 23) T. Onuma, *Master's thesis of Gunma University* (2004).
- 24) Y. Asai, *Master's thesis of Gunma University* (2005).
- 25) B. D'Alo, G. Coppola, and B. Pallesi, *Polymer* **15**, 130-132 (1974).
- 26) J. L. Koenig and M. C. Agboatwalla, *J. Macromol. Sci.-Phy.* **B2(3)**, 391-420 (1968).
- 27) N. Tanaka, *Proceedings of the 5th Italian Conference on Chemical and Process Engineering* (Florence), 949-952 (2001).
- 28) N. Tanaka and H. Fujii, *J. Macromol. Sci.* **B42**, 621-628 (2003).