

# Homogeneous crystal nucleation in polymers

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## Abstract

© 2017 IOP Publishing Ltd. The pathway of crystal nucleation significantly influences the structure and properties of semi-crystalline polymers. Crystal nucleation is normally heterogeneous at low supercooling, and homogeneous at high supercooling, of the polymer melt. Homogeneous nucleation in bulk polymers has been, so far, hardly accessible experimentally, and was even doubted to occur at all. This topical review summarizes experimental findings on homogeneous crystal nucleation in polymers. Recently developed fast scanning calorimetry, with cooling and heating rates up to  $10^6 \text{ K s}^{-1}$ , allows for detailed investigations of nucleation near and even below the glass transition temperature, including analysis of nuclei stability. As for other materials, the maximum homogeneous nucleation rate for polymers is located close to the glass transition temperature. In the experiments discussed here, it is shown that polymer nucleation is homogeneous at such temperatures. Homogeneous nucleation in polymers is discussed in the framework of the classical nucleation theory. The majority of our observations are consistent with the theory. The discrepancies may guide further research, particularly experiments to progress theoretical development. Progress in the understanding of homogeneous nucleation is much needed, since most of the modelling approaches dealing with polymer crystallization exclusively consider homogeneous nucleation. This is also the basis for advancing theoretical approaches to the much more complex phenomena governing heterogeneous nucleation.

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## Keywords

classical nucleation theory (CNT), crystallization, fast scanning calorimetry (FSC), growth, nucleation, polymers

## References

- [1] Hoffman J D, Davis G T and Lauritzen J I 1976 *Treatise on Solid State Chemistry: Volume 3 Crystalline and Noncrystalline Solids* ed N B Hannay (Berlin: Springer) pp 497-614
- [2] Wunderlich B 1976 *Macromolecular Physics* vol 2 (New York: Academic)
- [3] Armistead K, Goldbeck-Wood G and Keller A 1992 *Polymer crystallization theories* *Adv. Polym. Sci.* 100 219-312
- [4] Meyer H 2003 *Structure Formation and Chain-Folding in Supercooled Polymer Melts. Some Ideas from MD Simulations with a Coarse-Grained Model*. *Polymer Crystallization, Lecture Notes in Physics* vol 606 ed G Reiter and J U Sommer (Berlin, Heidelberg: Springer) pp 177-95
- [5] Muthukumar M 2003 *Molecular modelling of nucleation in polymers* *Phil. Trans. R. Soc. A* 361 539-56
- [6] Muthukumar M 2004 *Advances in Chemical Physics* (New York: Wiley) pp 1-63

- [7] Muthukumar M 2005 Modeling polymer crystallization *Adv. Polym. Sci.* 191 241-74
- [8] Sommer J-U and Luo C 2010 Molecular dynamics simulations of semicrystalline polymers: crystallization, melting, and reorganization *J. Polym. Sci. B* 48 2222-32
- [9] Luo C and Sommer J-U 2015 Role of thermal history and entanglement related thickness selection in polymer crystallization *ACS Macro Lett.* 5 30-4
- [10] Schmelzer J W P and Abyzov A S 2016 Crystallization of glass-forming liquids: specific surface energy *J. Chem. Phys.* 145 064512
- [11] Schmelzer J W P and Abyzov A S 2016 Crystallization of glass-forming liquids: thermodynamic driving force *J. Non-Cryst. Solids* 449 41-9
- [12] Zhang M, Guo B-H and Xu J 2017 A review on polymer crystallization theories *Crystals* 7 4
- [13] Lai S L, Ramanath G, Allen L H, Infante P and Ma Z 1995 High-speed (10(4)-degrees-C/S) scanning microcalorimetry with monolayer sensitivity (J/M(2)) *Appl. Phys. Lett.* 67 1229-31
- [14] Adamovsky S A, Minakov A A and Schick C 2003 Scanning microcalorimetry at high cooling rate *Thermochim. Acta* 403 55-63
- [15] Lopeandía A F, Cerdó L I, Clavaguera-Mora M T, Arana L R, Jensen K F, Muñoz F J and Rodríguez-Viejoa J 2005 Sensitive power compensated scanning calorimeter for analysis of phase transformations in small samples *Rev. Sci. Instrum.* 76 065104
- [16] Schick C and Mathot V 2016 *Fast Scanning Calorimetry* (Berlin: Springer)
- [17] Mileva D, Androsch R, Zhuravlev E and Schick C 2012 Morphology of mesophase and crystals of polyamide 6 prepared in a fast scanning chip calorimeter *Polymer* 53 3994-4001
- [18] Mileva D, Kolesov I and Androsch R 2012 Morphology of cold-crystallized polyamide 6 *Colloid Polym. Sci.* 290 971-8
- [19] Halpin J C and Kardos J L 1976 The Halpin-Tsai equations: a review *Polym. Eng. Sci.* 16 344-52
- [20] Doyle M J 2000 On the effect of crystallinity on the elastic properties of semicrystalline polyethylene *Polym. Eng. Sci.* 40 330-5
- [21] Bédoui F, Diani J and Régnier G 2004 Micromechanical modeling of elastic properties in polyolefins *Polymer* 45 2433-42
- [22] Zia Q, Radusch H-J and Androsch R 2009 Deformation behavior of isotactic polypropylene crystallized via a mesophase *Polym. Bull.* 63 755-71
- [23] Mileva D, Zia Q and Androsch R 2010 Tensile properties of random copolymers of propylene with ethylene and 1-butene: effect of crystallinity and crystal habit *Polym. Bull.* 65 623-34
- [24] Starkweather H W and Brooks R E 1959 Effect of spherulites on the mechanical properties of nylon 66 *J. Appl. Polym. Sci.* 1 236-9
- [25] Way J L, Atkinson J R and Nutting J 1974 The effect of spherulite size on the fracture morphology of polypropylene *J. Mater. Sci.* 9 293-9
- [26] Perkins W G 1999 Polymer toughness and impact resistance *Polym. Eng. Sci.* 39 2445-60
- [27] Hawkins S W and Richards R B 1949 Light transmission and the formation and decay of spherulites in polythene *J. Polym. Sci.* 4 515-22
- [28] Pritchard R 1964 The transparency of crystalline polymers *SPE Trans.* 4 66-71
- [29] Stein R S and Prud'Homme R 1971 Origin of polyethylene transparency *J. Polym. Sci. B* 9 595-8
- [30] Bheda J H and Spruiell J E 1986 The effect of process and polymer variables on the light transmission properties of polypropylene tubular blown films *Polym. Eng. Sci.* 26 736-45
- [31] Shibayama M, Imamura K-I, Katoh K and Nomura S 1991 Transparency of recycled polypropylene film *J. Appl. Polym. Sci.* 42 1451-8
- [32] Losev Y P 1997 *Transparent Polyolefins* (Boca Raton, FL: CRC Press)
- [33] Blomenhofer M, Ganzleben S, Hanft D, Schmidt H-W, Kristiansen M, Smith P, Stoll K, Mäder D and Hoffmann K 2005 'Designer' nucleating agents for polypropylene *Macromolecules* 38 3688-95
- [34] Tenma M, Mieda N, Takamatsu S and Yamaguchi M 2008 Structure and properties for transparent polypropylene containing sorbitol-based clarifier *J. Polym. Sci. B* 46 41-7
- [35] Menyhárd A, Gahleitner M, Varga J, Bernreitner K, Jääskeläinen P, Øysæd H and Pukánszky B 2009 The influence of nucleus density on optical properties in nucleated isotactic polypropylene *Eur. Polym. J.* 45 3138-48
- [36] Mileva D, Androsch R and Radusch H J 2009 Effect of the structure on light transmission in isotactic polypropylene and random propylene-1-butene copolymers *Polym. Bull.* 62 561-71
- [37] Zia Q, Androsch R and Radusch H-J 2010 Effect of the structure at the micrometer and nanometer scales on the light transmission of isotactic polypropylene *J. Appl. Polym. Sci.* 117 1013-20

- [38] Funaki A, Kanai T, Saito Y and Yamada T 2010 Analysis of contributing factors to production of highly transparent isotactic polypropylene extrusion sheets. Part I Polym. Eng. Sci. 50 2356-65
- [39] Funaki A, Kondo K and Kanai T 2011 Analysis of contributing factors to production of highly transparent isotactic polypropylene extrusion sheets. Part 2 Polym. Eng. Sci. 51 1068-77
- [40] Kolesov I, Mileva D and Androsch R 2014 Mechanical behavior and optical transparency of polyamide 6 of different morphology formed by variation of the pathway of crystallization Polym. Bull. 71 581-93
- [41] Strobl G 2007 The Physics of Polymers (Berlin: Springer)
- [42] Wunderlich B 2003 Reversible crystallization and the rigid-amorphous phase in semicrystalline macromolecules Prog. Polym. Sci. 28 383-450
- [43] Wunderlich B 2012 Termination of crystallization or ordering of flexible, linear macromolecules J. Therm. Anal. Calorim. 109 1117-32
- [44] Gutzow I S and Schmelzer J W P 2013 The Vitreous State Thermodynamics, Structure, Rheology, and Crystallization (Heidelberg: Springer)
- [45] Volmer M and Weber A 1926 Tröpfchenbildung in Dämpfen Z. Phys. Chem. 119 227
- [46] Becker R and Döring W 1935 Kinetische Behandlung der Keimbildung in übersättigten Dämpfen Ann. Phys. 24 719-52
- [47] Stranski I N and Kaischew R 1935 Gleichgewichtsform und Wachstumsform der Kristalle Ann. Phys., Lpz. 415 330-8
- [48] Turnbull D and Fisher J C 1949 Rate of nucleation in condensed systems J. Chem. Phys. 17 71-3
- [49] Schmelzer J W P, Abyzov A S and Baidakov V G 2017 Time of formation of the first supercritical nucleus, time-lag, and the steady-state nucleation rate Int. J. Appl. Glass Sci. 8 48-60
- [50] Androsch R, Schick C and Schmelzer J W P 2014 Sequence of enthalpy relaxation, homogeneous crystal nucleation and crystal growth in glassy polyamide 6 Eur. Polym. J. 53 100-8
- [51] Zhuravlev E, Schmelzer J W P, Wunderlich B and Schick C 2011 Kinetics of nucleation and crystallization in poly(epsilon caprolactone) (PCL) Polymer 52 1983-97
- [52] Schmelzer J W P 2010 On the determination of the kinetic pre-factor in classical nucleation theory J. Non-Cryst. Solids 356 2901-7
- [53] Schmelzer J W P, Abyzov A S, Fokin V M, Schick C and Zanotto E D 2015 Crystallization in glass-forming liquids: effects of decoupling of diffusion and viscosity on crystal growth J. Non-Cryst. Solids 429 45-53
- [54] Pavlov P A 1991 Homogeneous nucleation sites Fluid Mech. - Sov. Res. 20 98-107
- [55] Gibbs J W 1874-1878 Transactions of the Connecticut Academy of Sciences (New Haven: Tuttle, Murehouse & Taylor, Printers) pp 108-248
- [56] van der Waals J D 1893 The thermodynamic theory of capillarity under the hypothesis of a continuous variation of density Verh. K. Akad. Wet. 1 1 56
- [57] Rowlinson J S 1979 Translation of J D van der Waals' 'the thermodynamik theory of capillarity under the hypothesis of a continuous variation of density' J. Stat. Phys. 20 197-200
- [58] Herlach D, Galenko P and Holland-Moritz D 2007 Metastable Solids from Undercooled Melts vol 10 (Amsterdam: Elsevier)
- [59] Schmelzer J W P, Schmelzer J Jr and Gutzow I S 2000 Reconciling Gibbs and van der Waals: a new approach to nucleation theory J. Chem. Phys. 112 3820-31
- [60] Schmelzer J W P, Fokin V M, Abyzov A S, Zanotto E D and Gutzow I 2010 How do crystals form and grow in glass-forming liquids: Ostwald's rule of stages and beyond Int. J. Appl. Glass Sci. 1 16-26
- [61] Hillert M 1956 A theory of nucleation for solid metallic solutions PhD Thesis Massachusetts Institute of Technology, Cambridge
- [62] Cahn J W and Hilliard J E 1959 Free energy of a nonuniform system. III. Nucleation in a two-component incompressible fluid J. Chem. Phys. 31 688-99
- [63] Schmelzer J W P, Boltachev G S and Baidakov V G 2006 Classical and generalized Gibbs' approaches and the work of critical cluster formation in nucleation theory J. Chem. Phys. 124 194503
- [64] Hobstetter J N 1949 Stable transformation nuclei in solids Trans. Am. Inst. Min. Metall. Eng. 180 121-30
- [65] Scheil E 1952 Bemerkung über die Konzentration von Keimen bei ihrer Ausscheidung aus übersättigten Mischkristallen Z. Met.kd 43 40-1
- [66] Cahn J W 1998 Selected Works of J. W. Cahn ed W C Carter and W C Johnson (Warrendale, USA: The Minerals, Metals & Materials Society) pp 1-8
- [67] Baidakov V G, Boltashev G S and Schmelzer J W P 2000 Comparison of different approaches to the determination of the work of critical cluster formation J. Colloid Interface Sci. 231 312-21
- [68] Ostwald W 1897 Studien über die Bildung und Umwandlung fester Körper Z. Phys. Chem. 22 286-330

- [69] Stranski I N and Totomanov D 1933 Keimbildungsgeschwindigkeit und Ostwaldsche Stufenregel Z. Phys. Chem. 163A 399
- [70] Strobl G 2006 Crystallization and melting of bulk polymers: new observations, conclusions and a thermodynamic scheme Prog. Polym. Sci. 31 398-442
- [71] Wulff G 1901 Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Kristallflächen Z. Kristallogr. Mineral. 34 449-530
- [72] Dirksen J A and Ring T A 1991 Fundamentals of crystallization: kinetic effects on particle size distributions and morphology Chem. Eng. Sci. 46 2389-427
- [73] Schmelzer J W P, Abyzov A S and Fokin V M 2016 Thermodynamic aspects of pressure-induced crystallization: Kauzmann pressure Int. J. Appl. Glass Sci. 7 474-85
- [74] Fokin V M, Abyzov A S, Zanotto E D, Cassar D R, Rodrigues A M and Schmelzer J W P 2016 Crystal nucleation in glass-forming liquids: variation of the size of the 'structural units' with temperature J. Non-Cryst. Solids 447 35-44
- [75] Abyzov A S, Fokin V M, Yuritsyn N S, Rodrigues A M and Schmelzer J W P 2017 The effect of heterogeneous structure of glass-forming liquids on crystal nucleation J. Non-Cryst. Solids 462 32-40
- [76] Schmelzer J W P 2012 Kinetic criteria of glass formation and the pressure dependence of the glass transition temperature J. Chem. Phys. 136 074512
- [77] Bourque A, Locker C R and Rutledge G C 2016 Molecular dynamics simulation of surface nucleation during growth of an alkane crystal Macromolecules 49 3619-29
- [78] Schmelzer J W P, Abyzov A S, Fokin V M, Schick C and Zanotto E D 2015 Crystallization of glass-forming liquids: maxima of nucleation, growth, and overall crystallization rates J. Non-Cryst. Solids 429 24-32
- [79] Tammann G 1898 Über die Abhängigkeit der Zahl der Kerne, welche sich in verschiedenen unterkühlten Flüssigkeiten bilden, von der Temperatur Z. Phys. Chem. 25 441-79
- [80] Lifshitz I M and Slyozov V V 1961 The kinetics of precipitation from supersaturated solid solutions J. Phys. Chem. Solids 19 35-50
- [81] Fokin V M, Abyzov A S, Schmelzer J W P and Zanotto E D 2010 Stress induced pore formation and phase selection in a crystallizing stretched glass J. Non-Cryst. Solids 356 1679-88
- [82] Mathot V B F 1994 Calorimetry and Thermal Analysis of Polymers (München: Hanser Publishers)
- [83] Wunderlich B 2005 Thermal Analysis of Polymeric Materials (Berlin: Springer)
- [84] Schick C 2009 Differential scanning calorimetry (DSC) of semicrystalline polymers Anal. Bioanal. Chem. 395 1589-611
- [85] Fokin V M, Cabral A A, Reis R M C V, Nascimento M L F and Zanotto E D 2010 Critical assessment of DTA-DSC methods for the study of nucleation kinetics in glasses J. Non-Cryst. Solids 356 358-67
- [86] Kolmogorov A N 1937 On the statistical theory of crystallization of metals Izv. Akad. Nauk SSSR 3 355-9
- [87] Avrami M 1939 Kinetics of phase change. I General theory J. Chem. Phys. 7 1103-12
- [88] Johnson W A and Mehl R 1939 Reaction kinetics in processes of nucleation and growth Trans. AIME 135 416-58
- [89] Avrami M 1940 Kinetics of phase change. II Transformation-time relations for random distribution of nuclei J. Chem. Phys. 8 212-24
- [90] Long Y, Shanks R A and Stachurski Z H 1995 Kinetics of polymer crystallisation Prog. Polym. Sci. 20 651-701
- [91] Lacmann R 1961 Über die Kristallisation auf Unterlagen und die Keimbildungsarbeiten Z. Kristallogr. 116 13-26
- [92] Vidotto G, Levy D and Kovacs A J 1969 Cristallisation et fusion des polymères autoensemencés I. Polybutène-1, polyéthylène et polyoxyéthylène de haute masse moléculaire Kolloid. Z. Z. Polym. 230 289-305
- [93] Blundell D J, Keller A and Kovacs A J 1966 A new self-nucleation phenomenon and its application to the growing of polymer crystals from solution J. Polym. Sci. C 4 481
- [94] Blundell D J and Keller A 1968 Nature of self-seeding polyethylene crystal nuclei J. Macromol. Sci. - Phys. B 2 301-36
- [95] Fillon B, Lotz B, Thierry A and Wittmann J C 1993 Self-nucleation and enhanced nucleation of polymers. Definition of a convenient calorimetric 'efficiency scale' and evaluation of nucleating additives in isotactic polypropylene ( $\alpha$  phase) J. Polym. Sci. B 31 1395-405
- [96] Müller A, Hernández Z, Arnal M and Sánchez J 1997 Successive self-nucleation/annealing (SSA): a novel technique to study molecular segregation during crystallization Polym. Bull. 39 465-72
- [97] Muthukumar M 2016 Communication: theory of melt-memory in polymer crystallization J. Chem. Phys. 145 031105
- [98] Cavallo D, Lorenzo A T and Müller A J 2016 Probing the early stages of thermal fractionation by successive self-nucleation and annealing performed with fast scanning chip-calorimetry J. Polym. Sci. B 54 2200-9

- [99] Michell R M, Mugica A, Zubitur M and Müller A J 2017 Self-Nucleation of Crystalline Phases Within Homopolymers, Polymer Blends, Copolymers, and Nanocomposites, Advances in Polymer Sciences vol. 276 (Berlin: Springer) pp 215-56
- [100] Sangroniz L, Cavallo D, Santamaria A, Müller A J and Alamo R G 2017 Thermorheologically complex self-seeded melts of propylene-ethylene copolymers *Macromolecules* 50 642-51
- [101] Fillon B, Wittmann J C, Lotz B and Thierry A 1993 Self-nucleation and recrystallization of isotactic polypropylene (a phase) investigated by differential scanning calorimetry *J. Polym. Sci. B* 31 1383-93
- [102] Wunderlich B and Cormier C M 1966 Seeding of supercooled polyethylene with extended chain crystals *J. Phys. Chem.* 70 1844-9
- [103] Wunderlich B and Mehta A 1974 Macromolecular nucleation *J. Polym. Sci. B* 12 255-63
- [104] Keller A 1979 Crystalline polymers; an introduction *Faraday Discuss. Chem. Soc.* 68 145-66
- [105] Yeh G S Y and Geil P H 1967 Crystallization of polyethylene terephthalate from the glassy amorphous state *J. Macromol. Sci. - Phys. B* 1 235-49
- [106] Ogawa T, Miyaji H and Asai K 1985 Nodular structure of polypropylene *J. Phys. Soc. Japan* 54 3668-70
- [107] Bensason S, Minick J, Moet A, Chum S, Hiltner A and Baer E 1996 Classification of homogeneous ethylene-octene copolymers based on comonomer content *J. Polym. Sci. B* 34 1301-15
- [108] Mathot V B F, Scherrenberg R L and Pijpers T F J 1998 Metastability and order in linear, branched and copolymerized polyethylenes *Polymer* 39 4541-59
- [109] Alizadeh A, Richardson L, Xu J, McCartney S, Marand H, Cheung Y W and Chum S 1999 Influence of structural and topological constraints on the crystallization and melting behavior of polymers. 1. Ethylene/1-octene copolymers *Macromolecules* 32 6221-35
- [110] Poon B, Rogunova M, Chum S P, Hiltner A and Baer E 2004 Classification of homogeneous copolymers of propylene and 1-octene based on comonomer content *J. Polym. Sci. B* 42 4357-70
- [111] Kolesov I S, Androsch R and Radusch H J 2005 Effect of crystal morphology and crystallinity on the mechanical  $\alpha$ - and  $\beta$ -relaxation processes of short-chain branched polyethylene *Macromolecules* 38 445-53
- [112] Zia Q, Androsch R, Radusch H J and Piccarolo S 2006 Morphology, reorganization and stability of mesomorphic nanocrystals in isotactic polypropylene *Polymer* 47 8163-72
- [113] Zia Q, Androsch R, Radusch H-J and Ingoliç E 2008 Crystal morphology of rapidly cooled isotactic polypropylene: a comparative study by TEM and AFM *Polym. Bull.* 60 791-8
- [114] Bassett D C 1981 Principles of Polymer Morphology (Cambridge: Cambridge University Press)
- [115] Bassett D C, Frank F C and Keller A 1994 Lamellae and their organization in melt-crystallized polymers *Phil. Trans. R. Soc. Lond. A* 348 29-43
- [116] Magill J H 2001 Spherulites: a personal perspective *J. Mater. Sci.* 36 3143-64
- [117] Hoffman J D and Lauritzen J I Jr 1961 Crystallization of bulk polymers with chain folding: theory of growth of lamellar spherulites *J. Res. Natl Bur. Stand.* 65A 297-336
- [118] Hoffman J D 1964 Theoretical Aspects of Polymer Crystallization with Chain Folds: Bulk Polymers
- [119] Lauritzen J I and Hoffman J D 1973 Extension of theory of growth of chain-folded polymer crystals to large undercoolings *J. Appl. Phys.* 44 4340-52
- [120] Strobl G 2000 From the melt via mesomorphic and granular crystalline layers to lamellar crystallites: a major route followed in polymer crystallization? *Eur. Phys. J. E* 3 165-83
- [121] Kim H G and Robertson R E 1998 A new approach for estimating the recrystallization rate and equilibrium melting temperature *J. Polym. Sci. B* 36 133-41
- [122] Kim H G and Robertson R E 1998 Multiple melting endotherms in isothermally melt-crystallized poly(butylene terephthalate) *J. Polym. Sci. B* 36 1757-67
- [123] Minakov A A, Mordvintsev D A and Schick C 2004 Melting and reorganization of poly(ethylene terephthalate) on fast heating (1 000 K s<sup>-1</sup>) *Polymer* 45 3755-63
- [124] Minakov A A, Mordvintsev D A and Schick C 2005 Isothermal reorganization of poly(ethylene terephthalate) revealed by fast calorimetry (1000 K s<sup>-1</sup>; 5 ms) *Faraday Discuss.* 128 261-70
- [125] Minakov A A, Mordvintsev D A, Tol R and Schick C 2006 Melting and reorganization of the crystalline fraction and relaxation of the rigid amorphous fraction of isotactic polystyrene on fast heating (30 000 K min<sup>-1</sup>) *Thermochim. Acta* 442 25-30
- [126] Furushima Y, Kumazawa S, Umetsu H, Toda A, Zhuravlev E and Schick C 2017 Melting and recrystallization kinetics of poly(butylene terephthalate) *Polymer* 109 307-14
- [127] Minakov A, Wurm A and Schick C 2007 Superheating in linear polymers studied by ultrafast nanocalorimetry *Eur. Phys. J. E* 23 43-53
- [128] Toda A, Kojima I and Hikosaka M 2008 Melting kinetics of polymer crystals with an entropic barrier *Macromolecules* 41 120-7

- [129] Toda A, Taguchi K, Sato K, Nozaki K, Maruyama M, Tagashira K and Konishi M 2013 Melting kinetics of it-polypropylene crystals over wide heating rates *J. Therm. Anal. Calorim.* 113 1231-7
- [130] Furushima Y, Nakada M, Murakami M, Yamane T, Toda A and Schick C 2015 Method for calculation of the lamellar thickness distribution of not-reorganized linear polyethylene using fast scanning calorimetry in heating *Macromolecules* 48 8831-7
- [131] Toda A 2016 Heating rate dependence of melting peak temperature examined by DSC of heat flux type *J. Therm. Anal. Calorim.* 123 1795-808
- [132] Toda A, Androsch R and Schick C 2016 Insights into polymer crystallization and melting from fast scanning chip calorimetry *Polymer* 91 239-63
- [133] Oxtoby D W 1992 Homogeneous nucleation: theory and experiment *J. Phys.: Condens. Matter* 4 7627
- [134] Langhe D S, Hiltner A and Baer E 2011 Transformation of isotactic polypropylene droplets from the mesophase into the  $\alpha$ -phase *J. Polym. Sci. B* 49 1672-82
- [135] Mileva D, Androsch R, Cavallo D and Alfonso G C 2012 Structure formation of random isotactic copolymers of propylene and 1-hexene or 1-octene at rapid cooling *Eur. Polym. J.* 48 1082-92
- [136] Androsch R and Schick C 2017 Polymer Crystallization I ed F Auriemma et al (Berlin: Springer) pp 257-88
- [137] Mileva D, Androsch R, Zhuravlev E, Schick C and Wunderlich B 2012 Homogeneous nucleation and mesophase formation in glassy isotactic polypropylene *Polymer* 53 277-82
- [138] Qamer Z and René A 2009 Effect of atomic force microscope tip geometry on the evaluation of the crystal size of semicrystalline polymers *Meas. Sci. Technol.* 20 097003
- [139] Cormia R L, Price F P and Turnbull D 1962 Kinetics of crystal nucleation in polyethylene *J. Chem. Phys.* 37 1333-40
- [140] Burns J R and Turnbull D 1966 Kinetics of crystal nucleation in molten isotactic polypropylene *J. Appl. Phys.* 37 4021-6
- [141] Gornick F, Ross G S and Frolen L J 1967 Crystal nucleation in polyethylene: the droplet experiment *J. Polym. Sci. B* 18 79-91
- [142] Burns J R and Turnbull D 1968 Nucleation of crystallization in molten isotactic polybutene-1 *J. Polym. Sci. A-2* 6 775-82
- [143] Koutsky J A, Walton A G and Baer E 1967 Nucleation of polymer droplets *J. Appl. Phys.* 38 1832-9
- [144] Massa M V and Dalnoki-Veress K 2004 Homogeneous crystallization of poly(ethylene oxide) confined to droplets: the dependence of the crystal nucleation rate on length scale and temperature *Phys. Rev. Lett.* 92 255509
- [145] Massa M V, Carvalho J L and Dalnoki-Veress K 2006 Confinement effects in polymer crystal nucleation from the bulk to few-chain systems *Phys. Rev. Lett.* 97 247802
- [146] Carvalho J L and Dalnoki-Veress K 2010 Homogeneous bulk, surface, and edge nucleation in crystalline nanodroplets *Phys. Rev. Lett.* 105 237801
- [147] Massa M V, Lee M S M and Dalnoki-Veress K 2005 Crystal nucleation of polymers confined to droplets: memory effects *J. Polym. Sci. B* 43 3438-43
- [148] Carvalho J and Dalnoki-Veress K 2011 Surface nucleation in the crystallisation of polyethylene droplets *Eur. Phys. J. E* 34 1-6
- [149] Ghijsels A, Groesbeek N and Yip C W 1982 Multiple crystallization behaviour of polypropylene/thermoplastic rubber blends and its use in assessing blend morphology *Polymer* 23 1913-6
- [150] Arnal M L, Matos M E, Morales R A, Santana O O and Müller A J 1998 Evaluation of the fractionated crystallization of dispersed polyolefins in a polystyrene matrix *Macromol. Chem. Phys.* 199 2275-88
- [151] Santana O O and Müller A J 1994 Homogeneous nucleation of the dispersed crystallisable component of immiscible polymer blends *Polym. Bull.* 32 471-7
- [152] Arnal M L, Müller A J, Maiti P and Hikosaka M 2000 Nucleation and crystallization of isotactic poly(propylene) droplets in an immiscible polystyrene matrix *Macromol. Chem. Phys.* 201 2493-504
- [153] Uriguen J I, Bremer L, Mathot V and Groeninckx G 2004 Preparation of water-borne dispersions of polyolefins: new systems for the study of homogeneous nucleation of polymers *Polymer* 45 5961-8
- [154] Tol R T, Mathot V B F, Reynaers H, Goderis B and Groeninckx G 2005 Confined crystallization phenomena in immiscible polymer blends with dispersed micro-and nanometer sized PA6 droplets part 4: polymorphous structure and (meta)-stability of PA6 crystals formed in different temperature regions *Polymer* 46 2966-77
- [155] Tol R T, Minakov A A, Adamovsky S A, Mathot V B F and Schick C 2006 Metastability of polymer crystallites formed at low temperature studied by ultra fast calorimetry: polyamide 6 confined in sub-micrometer droplets versus bulk PA6 *Polymer* 47 2172-8
- [156] Sánchez M S, Mathot V, Poel G V, Groeninckx G and Bruls W 2006 Crystallization of polyamide confined in sub-micrometer droplets dispersed in a molten polyethylene matrix *J. Polym. Sci. B* 44 815-25

- [157] Ibarretxe J, Groeninckx G, Bremer L and Mathot V B F 2009 Quantitative evaluation of fractionated and homogeneous nucleation of polydisperse distributions of water-dispersed maleic anhydride-grafted-polypropylene micro- and nano-sized droplets *Polymer* 50 4584-95
- [158] Vonnegut B 1948 Variation with temperature of the nucleation rate of supercooled liquid tin and water drops *J. Colloid Sci.* 3 563-9
- [159] Turnbull D 1950 Formation of crystal nuclei in liquid metals *J. Appl. Phys.* 21 1022-8
- [160] Turnbull D 1950 Isothermal rate of solidification of small droplets of mercury and tin *J. Chem. Phys.* 18 768-9
- [161] Turnbull D 1952 Kinetics of solidification of supercooled liquid mercury droplets *J. Chem. Phys.* 20 411-24
- [162] Skripov V P 1974 *Metastable Liquids* (New York: Wiley)
- [163] Turnbull D and Cormia R L 1961 Kinetics of crystal nucleation in some normal alkane liquids *J. Chem. Phys.* 34 820-31
- [164] Turnbull D and Spaepen F 1978 Crystal nucleation and the crystal-melt interfacial tension in linear hydrocarbons *J. Polym. Sci. B* 63 237-43
- [165] Zhuravlev E, Madhavi V, Lustiger A, Androsch R and Schick C 2016 Crystallization of polyethylene at large undercooling *ACS Macro Lett.* 5 365-70
- [166] Barham P J, Jarvis D A and Keller A 1982 A new look at the crystallization of polyethylene. III. Crystallization from the melt at high supercoolings *J. Polym. Sci. Polym. Phys. Ed.* 20 1733-48
- [167] Alharbe L G, Register R A and Hobbs J K 2015 Orientation control and crystallization in a soft confined phase separated block copolymer *Macromolecules* 48 8831-7
- [168] Androsch R, Di Lorenzo M L, Schick C and Wunderlich B 2010 Mesophases in polyethylene, polypropylene, and poly(1-butene) *Polymer* 51 4639-62
- [169] De Santis F, Adamovsky S, Titomanlio G and Schick C 2007 Isothermal nanocalorimetry of isotactic polypropylene *Macromolecules* 40 9026-31
- [170] Duran H, Steinhart M, Butt H-J R and Floudas G 2011 From heterogeneous to homogeneous nucleation of isotactic poly(propylene) confined to nanoporous alumina *Nano Lett.* 11 1671-5
- [171] Kailas L, Vasilev C, Audinot J N, Migeon H N and Hobbs J K 2007 A real-time study of homogeneous nucleation, growth, and phase transformations in nanodroplets of low molecular weight isotactic polypropylene using AFM *Macromolecules* 40 7223-30
- [172] Lin M-C, Chen H-L, Lin W-F, Huang P-S and Tsai J-C 2012 Crystallization of isotactic polypropylene under the spatial confinement templated by block copolymer microdomains *J. Phys. Chem. B* 116 12357-71
- [173] Schmelzer J W P, Gokhman A R and Fokin V M 2004 Dynamics of first-order phase transitions in multicomponent systems: a new theoretical approach *J. Colloid Interface Sci.* 272 109-33
- [174] Schmelzer J W P, Abyzov A S and Möller J 2004 Nucleation versus spinodal decomposition in phase formation processes in multicomponent solutions *J. Chem. Phys.* 121 6900-17
- [175] Schmelzer J W P and Gutzow I S 2012 *Glasses and the Glass Transition* (New York: Wiley)
- [176] Reiter G, Castelein G and Sommer J U 2001 Direct visualization of random crystallization and melting in arrays of nanometer-size polymer crystals *Phys. Rev. Lett.* 87 226101
- [177] Müller A J, Balsamo V, Arnal M L, Jakob T, Schmalz H and Abetz V 2002 Homogeneous nucleation and fractionated crystallization in block copolymers *Macromolecules* 35 3048-58
- [178] Rottele A, Thurn-Albrecht T, Sommer J U and Reiter G 2003 Thermodynamics of formation, reorganization, and melting of confined nanometer-sized polymer crystals *Macromolecules* 36 1257-60
- [179] Müller A J, Balsamo V and Arnal M L 2005 Nucleation and crystallization in diblock and triblock copolymers *Adv. Polym. Sci.* 190 1-63
- [180] Hempel E, Budde H, Höring S and Beiner M 2005 Side chain crystallization in microphase-separated poly(styrene-block-octadecylmethacrylate) copolymers *Thermochim. Acta* 432 254-61
- [181] Lorenzo A T, Arnal M L, Müller A J, de Fierro A B and Abetz V 2006 Confinement effects on the crystallization and SSA thermal fractionation of the PE block within PE-b-PS diblock copolymers *Eur. Polymer J.* 42 516-33
- [182] Jiang K, Su Y, Xie B, Jiang S, Zhao Y and Wang D 2008 Effect of geometrical confinement on the nucleation and crystallization behavior of n-alkane mixtures *J. Phys. Chem. B* 112 16485-9
- [183] Michell R M, Lorenzo A T, Müller A J, Lin M-C, Chen H-L, Blaszczyk-Lezak I, Martín J and Mijangos C 2012 The crystallization of confined polymers and block copolymers infiltrated within alumina nanotube templates *Macromolecules* 5 1517-28
- [184] Suzuki Y, Duran H, Akram W, Steinhart M, Floudas G and Butt H-J 2013 Multiple nucleation events and local dynamics of poly(epsilon-caprolactone) (PCL) confined to nanoporous alumina *Soft Matter* 9 9189-98
- [185] Michell R M and Müller A J 2016 Confined crystallization of polymeric materials *Prog. Polym. Sci.* 54-5 183-213
- [186] Jin Y, Hiltner A and Baer E 2007 Fractionated crystallization of polypropylene droplets produced by nanolayer breakup *J. Polym. Sci. B* 45 1138-51

- [187] Suzuki Y, Duran H, Steinhart M, Butt H-J and Floudas G 2013 Homogeneous crystallization and local dynamics of poly(ethylene oxide) (PEO) confined to nanoporous alumina *Soft Matter* 9 2621-8
- [188] Li L, Liu J, Qin L, Zhang C, Sha Y, Jiang J, Wang X, Chen W, Xue G and Zhou D 2017 Crystallization kinetics of syndiotactic polypropylene confined in nanoporous alumina *Polymer* 110 273-83
- [189] Bosq N, Guigo N, Zhuravlev E and Sbirrazzuoli N 2013 Nonisothermal crystallization of polytetrafluoroethylene in a wide range of cooling rates *J. Phys. Chem. B* 117 3407-15
- [190] Androsch R, Iqbal H M N and Schick C 2015 Non-isothermal crystal nucleation of poly (l-lactic acid) *Polymer* 81 151-8
- [191] Schick C and Androsch R 2016 New insights into polymer crystallization by fast scanning chip calorimetry *Fast Scanning Calorimetry* ed V B F Mathot and C Schick (Berlin: Springer) pp 463-535
- [192] Androsch R and Di Lorenzo M L 2013 Kinetics of crystal nucleation of poly(l-lactic acid) *Polymer* 54 6882-5
- [193] Di Lorenzo M L 2006 The crystallization and melting processes of poly(l-lactic acid) *Macromol. Symp.* 234 176-83
- [194] Hendus H, Illers K H and Šimák P 1969 Kristallisation von amorphem 6-Polyamid im Glasübergangsbereich *Kolloid. Z. Z. Polym.* 235 1244-6
- [195] Illers K H 1971 Geordnete Strukturen in 'amorphem' Polyäthylenterephthalat *Kolloid. Z. Z. Polym.* 245 393-8
- [196] Fokin V M, Zanotto E D, Yuritsyn N S and Schmelzer J W P 2006 Homogeneous crystal nucleation in silicate glasses: a 40 years perspective *J. Non-Cryst. Solids* 352 2681-714
- [197] Zhuravlev E, Schmelzer J W P, Abyzov A S, Fokin V M, Androsch R and Schick C 2015 Experimental test of Tammann's nuclei development approach in crystallization of macromolecules *Cryst. Growth Des.* 15 786-98
- [198] Androsch R, Schick C and Rhoades A M 2015 Application of Tammann's two-stage crystal nuclei development method for analysis of the thermal stability of homogeneous crystal nuclei of poly (ethylene terephthalate) *Macromolecules* 48 8082-9
- [199] Bove L, D'Aniello C, Gorraso G, Guadagno L and Vittoria V 1997 Influence of ageing on the cold crystallization of glassy poly(ethyleneterephthalate) *Polym. Bull.* 38 579-85
- [200] Zhang T, Hu J, Duan Y, Pi F and Zhang J 2011 Physical aging enhanced mesomorphic structure in melt-quenched poly(l-lactic acid) *J. Phys. Chem. B* 115 13835-41
- [201] Hay J N and Mills P J 1982 The use of differential scanning calorimetry to study polymer crystallization kinetics *Polymer* 23 1380-4
- [202] Chan T W and Isayev A I 1994 Quiescent polymer crystallization: modelling and measurements *Polym. Eng. Sci.* 34 461-71
- [203] Avrami M 1941 Granulation, phase change, and microstructure kinetics of phase change. III *J. Chem. Phys.* 9 177-84
- [204] Lorenzo A T, Arnal M L, Albuerne J and Müller A J 2007 DSC isothermal polymer crystallization kinetics measurements and the use of the Avrami equation to fit the data: guidelines to avoid common problems *Polym. Test.* 26 222-31
- [205] Abyzov A S, Fokin V M, Yuritsyn N S, Rodrigues A M and Schmelzer J W P 2017 The effect of heterogeneous structure of glass-forming liquids on crystal nucleation *J. Non-Cryst. Solids* 462 32-40
- [206] Vyazovkin S and Sbirrazzuoli N 2004 Isoconversional approach to evaluating the Hoffman-Lauritzen parameters ( $U^*$  and  $K_g$ ) from the overall rates of nonisothermal crystallization *Macromol. Rapid Commun.* 25 733-8
- [207] Adamovsky S and Schick C 2004 Ultra-fast isothermal calorimetry using thin film sensors *Thermochim. Acta* 415 1-7
- [208] Minakov A A, Adamovsky S A and Schick C 2005 Non adiabatic thin-film (chip) nanocalorimetry *Thermochim. Acta* 432 177-85
- [209] Pijpers M F J, Mathot V B F, Goderis B, Scherrenberg R and van der Vegte E 2002 High-speed calorimetry for the analysis of kinetics of vitrification, crystallization and melting of macromolecule *Macromolecules* 35 3601-13
- [210] Kolesov I S, Androsch R and Radusch H J 2004 Non-isothermal crystallization of polyethylenes as function of cooling rate and concentration of short chain branches *J. Therm. Anal. Calorim.* 78 885-95
- [211] Ding Z M and Spruiell J E 1996 An experimental method for studying nonisothermal crystallization of polymers at very high cooling rates *J. Polym. Sci. B* 34 2783-804
- [212] Boyer S A E and Haudin J M 2010 Crystallization of polymers at constant and high cooling rates: a new hot-stage microscopy set-up *Polym. Test.* 29 445-52
- [213] Märtsönen T, Ots A, Krumme A and Löhmus A 2010 Development of a faster hot-stage for microscopy studies of polymer crystallization *Polym. Test.* 29 127-31
- [214] Kamal M R and Chu E 1983 Isothermal and nonisothermal crystallization of polyethylene *Polym. Eng. Sci.* 23 27-31

- [215] Minakov A A and Schick C 2007 Ultrafast thermal processing and nanocalorimetry at heating and cooling rates up to 1 MK s<sup>-1</sup> Rev. Sci. Instrum. 78 073902-10
- [216] van Herwaarden S, Iervolino E, van Herwaarden F, Wijffels T, Leenaers A and Mathot V 2011 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 522 46-52
- [217] Zhuravlev E and Schick C 2010 Fast scanning power compensated differential scanning nano-calorimeter: 1. The device Thermochim. Acta 505 1-13
- [218] Zhuravlev E and Schick C 2010 Fast scanning power compensated differential scanning nano-calorimeter: 2. Heat capacity analysis Thermochim. Acta 505 14-21
- [219] Mathot V, Pyda M, Pijpers T, Vanden Poel G, van de Kerkhof E, van Herwaarden S, van Herwaarden F and Leenaers A 2011 The flash DSC 1, a power compensation twin-type, chip-based fast scanning calorimeter (FSC): first findings on polymers Thermochim. Acta 522 36-45
- [220] Poel G, Istrate D, Magon A and Mathot V 2012 Performance and calibration of the flash DSC 1, a new, MEMS-based fast scanning calorimeter J. Therm. Anal. Calorim. 110 1533-46
- [221] Minakov A A and Schick C 2015 Dynamics of the temperature distribution in ultra-fast thin-film calorimeter sensors Thermochim. Acta 603 205-17
- [222] Minakov A A and Schick C 2016 Heat conduction in ultrafast thin-film nanocalorimetry Thermochim. Acta 640 42-51
- [223] van Herwaarden A W 2005 Overview of calorimeter chips for various applications Thermochim. Acta 432 192-201
- [224] Zhuravlev E and Schick C 2016 Fast Scanning Calorimetry ed C Schick and V Mathot (Cham: Springer International Publishing) pp 81-104
- [225] Zhuravlev E, Wurm A, Pötschke P, Androsch R, Schmelzer J W P and Schick C 2014 Kinetics of nucleation and crystallization of poly( $\epsilon$ -caprolactone) - multiwalled carbon nanotube composites Eur. Polym. J. 52 1-11
- [226] Kadiyala R K and Angell C A 1984 Separation of nucleation from crystallization kinetics by two step calorimetry experiments Colloids Surf. 11 341-51
- [227] Okamoto N and Oguni M 1996 Discovery of crystal nucleation proceeding much below the glass transition temperature in a supercooled liquid Solid State Commun. 99 53-6
- [228] Salmeron Sanchez M, Mathot V B F, Vanden Poel G and Gomez Ribelles J L 2007 Effect of the cooling rate on the nucleation kinetics of poly(L-lactic acid) and its influence on morphology Macromolecules 40 7989-97
- [229] Wurm A, Zhuravlev E, Eckstein K, Jehnichen D, Pospiech D, Androsch R, Wunderlich B and Schick C 2012 Crystallization and homogeneous nucleation kinetics of poly( $\epsilon$ -caprolactone) (PCL) with different molar masses Macromolecules 45 3816-28
- [230] Wurm A, Soliman R and Schick C 2003 Early stages of polymer crystallization - a dielectric study Polymer 44 7467-76
- [231] Wunderlich B 1995 The ATHAS database on heat capacities of polymers Pure Appl. Chem. 67 1019-26 see on [www.springermaterials.com/docs/athas.html](http://www.springermaterials.com/docs/athas.html)
- [232] Kremer F and Schönals A 2002 Broadband Dielectric Spectroscopy (Heidelberg: Springer)
- [233] Oguni M 1997 Intra-cluster rearrangement model for the alpha-process in supercooled liquids, as opposed to cooperative rearrangement of whole molecules within a cluster J. Non-Cryst. Solids 210 171-7
- [234] Mehta A and Wunderlich B 1975 A study of molecular fractionation during the crystallization polymers Colloid Polym. Sci. 253 193-205
- [235] Hodge I M 1994 Enthalpy relaxation and recovery in amorphous materials (Review) J. Non-Cryst. Solids 169 211-66
- [236] DeBolt M A, Easteal A J, Macedo P B and Moynihan C T 1976 Analysis of structural relaxation in glass using rate heating data J. Am. Ceram. Soc. 59 16-21
- [237] Ramos A R, Hutchinson J M and Kovacs A J 1984 Isobaric thermal behavior of glasses during uniform cooling and heating. III. Predictions from the multiparameter KAHR model J. Polym. Sci. Polym. Phys. Ed. 22 1655-95
- [238] Chang S S, Horman J A and Bestul A B 1967 Heat capacities and related thermal data for diethyl phthalate crystal, glass, and liquid to 360 °K J. Res. Natl Bur. Stand. A 71A 293-305
- [239] Wang Y and Mano J F 2006 Effect of structural relaxation at physiological temperature on the mechanical property of poly(L-lactic acid) studied by microhardness measurements J. Appl. Polym. Sci. 100 2628-33
- [240] Toda A, Taguchi K, Nozaki K and Konishi M 2014 Melting behaviors of polyethylene crystals: an application of fast-scan DSC Polymer 55 3186-94
- [241] Furushima Y, Toda A, Rousseaux V, Bailly C, Zhuravlev E and Schick C 2016 Quantitative understanding of two distinct melting kinetics of an isothermally crystallized poly(ether ether ketone) Polymer 99 97-104

- [242] Furushima Y, Nakada M, Ishikiriyama K, Toda A, Androsch R, Zhuravlev E and Schick C 2016 Two crystal populations with different melting/reorganization kinetics of isothermally crystallized polyamide 6 *J. Polym. Sci. B* 54 2126-38
- [243] Kolesov I, Mileva D, Androsch R and Schick C 2011 Structure formation of polyamide 6 from the glassy state by fast scanning chip calorimetry *Polymer* 52 5156-65
- [244] Mileva D, Androsch R, Zhuravlev E, Schick C and Wunderlich B 2011 Formation and reorganization of the mesophase of random copolymers of propylene and 1-butene *Polymer* 52 1107-15
- [245] Schmelzer J W P and Schick C 2012 Dependence of crystallization processes of glass-forming melts on melt history: a theoretical approach to a quantitative treatment *Phys. Chem. Glass. - Eur. J. Glass Sci. Technol. B* 53 99-106
- [246] Mollova A, Androsch R, Mileva D, Schick C and Benhamida A 2013 Effect of supercooling on crystallization of polyamide 11 *Macromolecules* 46 828-35
- [247] Androsch R and Di Lorenzo M L 2013 Crystal nucleation in glassy poly(l-lactic acid) *Macromolecules* 46 6048-56
- [248] Papageorgiou D G, Zhuravlev E, Papageorgiou G Z, Bikaris D, Chrissafis K and Schick C 2014 Kinetics of nucleation and crystallization in poly(butylene succinate) nanocomposites *Polymer* 55 6725-34
- [249] Schick C, Zhuravlev E, Androsch R, Wurm A and Schmelzer J W P 2014 Influence of Thermal Prehistory on Crystal Nucleation and Growth in Polymers, Glass - Selected Properties and Crystallization ed J W P Schmelzer (Berlin, Boston: De Gruyter) pp 1-93
- [250] Wurm A, Herrmann A, Cornelius M, Zhuravlev E, Pospiech D, Nicula R and Schick C 2015 Temperature dependency of nucleation efficiency of carbon nanotubes in PET and PBT *Macromol. Mater. Eng.* 300 637-49
- [251] Nishida K, Zhuravlev E, Yang B, Schick C, Shiraishi Y and Kanaya T 2015 Vitrification and crystallization of poly(butylene-2,6-naphthalate) *Thermochim. Acta* 603 110-5
- [252] Androsch R, Rhoades A M, Stolte I and Schick C 2015 Density of heterogeneous and homogeneous crystal nuclei in poly (butylene terephthalate) *Eur. Polym. J.* 66 180-9
- [253] Androsch R and Schick C 2016 Interplay between the relaxation of the glass of random l/d-lactide copolymers and homogeneous crystal nucleation: evidence for segregation of chain defects *J. Phys. Chem. B* 120 4522-8
- [254] Androsch R, Di Lorenzo M L and Schick C 2016 Crystal nucleation in random l/d-lactide copolymers *Eur. Polym. J.* 75 474-85
- [255] Rhoades A M, Wonderling N, Schick C and Androsch R 2016 Supercooling-controlled heterogeneous and homogenous crystal nucleation of polyamide 11 and its effect onto the crystal/mesophase polymorphism *Polymer* 106 29-34
- [256] Zhuravlev E, Schmelzer J W P, Androsch R and Schick C 2016 Experimental test of Tammann's nuclei development approach in crystallization of macromolecules *Int. Polym. Process.* 31 628-37
- [257] Stolte I, Androsch R, Di Lorenzo M L and Schick C 2013 Effect of aging the glass of isotactic polybutene-1 on form II nucleation and cold crystallization *J. Phys. Chem. B* 117 15196-203
- [258] Mileva D, Zia Q, Androsch R, Radusch H-J and Piccarolo S 2009 Mesophase formation in poly(propylene-ran-1-butene) by rapid cooling *Polymer* 50 5482-9
- [259] Mollova A, Androsch R, Mileva D, Gahleitner M and Funari S S 2013 Crystallization of isotactic polypropylene containing beta-phase nucleating agent at rapid cooling *Eur. Polym. J.* 49 1057-65
- [260] Gahleitner M, Mileva D, Androsch R, Gloger D, Tranchida D, Sandholzer M and Doshev P 2016 Crystallinity-based product design: utilizing the polymorphism of isotactic PP homo- and copolymers *Int. Polym. Process.* 31 618-27
- [261] Angell C A, MacFarlane D R and Oguni M 1986 The Kauzmann paradox, metastable liquids, and ideal glasses: a summary *Ann. New York Acad. Sci.* 484 241-7
- [262] Mamun A, Okui N and Gee R 2013 Enthalpy relaxation and nucleation density for isotactic polystyrene: annealing effect *Int. J. Eng. Res. Rev.* 1 29-36
- [263] Androsch R, Schick C and Di Lorenzo M L Kinetics of nucleation and growth of crystals of poly(l-lactic acid) *Adv. Polym. Sci.* in preparation (<https://doi.org/10.1007/12-2016-13>)
- [264] Mikhnevich G L and Browko J F 1938 Stability of the crystallization centers of an organic liquid at various temperatures and conclusions to be drawn therefrom concerning Tammann's method *Phys. Z. Sowjetunion* 13 9
- [265] Davis M 2000 Effect of the growth treatment on two-stage nucleation experiments: the 'flushing' effect *Glastech. Ber. Glass Sci. Technol.* 73 170-7
- [266] Davis M J 2001 Effect of the growth treatment on two-stage nucleation experiments *J. Am. Ceram. Soc.* 84 492-6
- [267] Nascimento M L F, Fokin V M, Zanotto E D and Abyzov A S 2011 Dynamic processes in a silicate liquid from above melting to below the glass transition *J. Chem. Phys.* 135 194703

- [268] Yamamoto T 2013 Molecular dynamics of polymer crystallization revisited: crystallization from the melt and the glass in longer polyethylene *J. Chem. Phys.* 139 054903
- [269] Schmelzer J W P, Boltachev G S and Abyzov A S 2013 Temperature of critical clusters in nucleation theory: generalized Gibbs' approach *J. Chem. Phys.* 139 034702-9
- [270] Schmelzer J W P, Abyzov A S, Fokin V M, Schick C and Zanotto E D 2015 Crystallization in glass-forming liquids: effects of fragility and glass transition temperature *J. Non-Cryst. Solids* 428 68-74
- [271] Allen L H, Ramanath G, Lai S L, Ma Z, Lee S, Allman D D J and Fuchs K P 1994 1000 000 'C/S thin film electrical heater: in situ resistivity measurements of Al and Ti/Si thin films during ultra rapid thermal annealing *Appl. Phys. Lett.* 64 417-9
- [272] Lai S L, Guo J Y, Petrova V, Ramanath G and Allen L H 1996 Size-dependent melting properties of small tin particles: nanocalorimetric measurements *Phys. Rev. Lett.* 77 99-102
- [273] Kelton K F and Greer A L 2010 Nucleation in Condensed Matter: Applications in Materials and Biology (Amsterdam: Elsevier)
- [274] Gao Y L, Zhuravlev E, Zou C D, Yang B, Zhai Q J and Schick C 2009 Calorimetric measurements of undercooling in single micron sized SnAgCu particles in a wide range of cooling rates *Thermochim. Acta* 482 1-7
- [275] Yang B, Gao Y L, Zou C D, Zhai Q J, Zhuravlev E and Schick C 2009 Repeated nucleation in an undercooled tin droplet by fast scanning calorimetry *Mater. Lett.* 63 2476-8
- [276] Yang B, Gao Y, Zou C, Zhai Q, Abyzov A, Zhuravlev E, Schmelzer J and Schick C 2011 Cooling rate dependence of undercooling of pure Sn single drop by fast scanning calorimetry *Appl. Phys. A* 104 189-96
- [277] Orava J, Greer A L, Gholipour B, Hewak D W and Smith C E 2012 Characterization of supercooled liquid Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and its crystallization by ultrafast-heating calorimetry *Nat. Mater.* 11 279-83
- [278] Yang B, Perepezko J H, Schmelzer J W P, Gao Y and Schick C 2014 Dependence of crystal nucleation on prior liquid overheating by differential fast scanning calorimeter *J. Chem. Phys.* 140 104513
- [279] Perepezko J H, Glendenning T W and Wang J-Q 2015 Nanocalorimetry measurements of metastable states *Thermochim. Acta* 603 24-8
- [280] Orava J, Hewak D W and Greer A L 2015 Fragile-to-strong crossover in supercooled liquid Ag-In-Sb-Te studied by ultrafast calorimetry *Adv. Funct. Mater.* 25 4851-8
- [281] Pogatscher S, Leutenegger D, Schawe J E K, Uggowitzer P J and Loffler J F 2016 Solid-solid phase transitions via melting in metals *Nat. Commun.* 7 11113
- [282] Yang B, Milkereit B, Zhang Y, Rometsch P A, Kessler O and Schick C 2016 Continuous cooling precipitation diagram of aluminium alloy AA7150 based on a new fast scanning calorimetry and interrupted quenching method *Mater. Charact.* 120 30-7