bution to the molar Kerr constant might be particularly sensitive to chain expansion in some polymers.

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Registry No. PVB, 25951-54-6; PVC, 9002-86-2; PS, 9003-53-6.

References and Notes

(1) Nagai, K. *J. Chem. Phys.* **1963**, *38*, 924.
(2) Jernigan, R. L.; Flory, P. J. *J. Chem. Phys.* **1969**, *50*, 4178.
(3) Flory, P. J. *Macromolecules* **1974**, *7*, 381.
(4) Mattice, W. L. *J. Chem. Phys.* **1987**, *87*, 5512.
(5) Saiz, E.; Riande, E.; Delgado, M. P.; Barrales-Rienda, J. M. *Macromolecules* **1982**, *15*, 1152.
(6) Mark, J. E. *J. Chem. Phys.* **1972**, *56*, 451.
(7) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(8) Tonelli, A. E. *Macromolecules* **1982**, *15*, 290.
(9) Carman, C. J.; Tarpley, A. R., Jr.; Goldstein, J. H. *Macromolecules* **1971**, *4*, 445.
(10) Cais, R. E.; Brown, W. L. *Macromolecules* **1980**, *13*, 801.
(11) Blasco Cantera, F.; Riande, E.; Almendro, J. P.; Saiz, E. *Macromolecules* **1981**, *14*, 138.
(12) Khanarian, G.; Schilling, F. C.; Cais, R. E.; Tonelli, A. E. *Macromolecules* **1983**, *16*, 287.
(13) Mattice, W. L.; Carpenter, D. K. *Macromolecules* **1984**, *17*, 625.
(14) Khanarian, G.; Stein, R. S. *Macromolecules* **1987**, *20*, 2858.

Notes

Anionic Polymerization of N-Substituted Maleimide. 4. "Living" Characteristics of Anionic Polymerization of *N*-Phenylmaleimide

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Introduction

A number of vinyl monomers possessing one carbonyl group such as acrylates and vinyl ketones can be polymerized with appropriate anionic initiators and the polymerization mechanism of such monomers has been studied quite intensively and systematically.[1-4] Some vinylidene monomers having the 1,1-dicarbonyl substituted or similar structure such as methylene malonates are also known to be easily polymerized with the initiators of low basicity.[5,6] However, for the anionic polymerization of vinylene monomers having a 1,2-dicarbonyl substituted structure, no detailed study has been carried out until 1985, not only on the mechanism of polymerization but also even on the polymerization reactivity of monomers to the initiators, because only a few vinylene monomers can be polymerized with basic initiators.[7-9] Dialkyl fumarates, for instance, are reported to give no polymer with typical anionic initiators such as butyllithium.[10] In previous papers[11-14] we first reported some new results that various anionic initiators—alkali-metal *tert*-butoxides, Grignard reagents, ate complexes, and organozinc compounds—as well as butyllithium, can polymerize *N*-phenylmaleimide (*N*-PMI) and *N*-ethylmaleimide and give corresponding homopolymers which are soluble in THF, 1,4-dioxane, dichloromethane, DMSO, and DMF, though an early report indicated that poly(*N*-PMI) produced with butyllithium could not be dissolved in any solvents. The polymerization of *N*-PMI initiated with potassium *tert*-butoxide in THF was suggestive of an extremely stable propagating species and afforded poly(*N*-PMI) in quantitative yield. Good agreement between the degree of polymerization and initial monomer/initiator molar ratio was also observed for alkali-metal *tert*-butoxides.

On the basis of these results, it seemed to be valuable to investigate the mechanism of anionic polymerization of *N*-PMI initiated with alkali-metal *tert*-butoxides in detail.

Experimental Section

Reagents. *N*-PMI (from Japan Catalytic Chemical Ind.) was purified by recrystallization several times from purified cyclohexane and dried in vacuo at room temperature. It was further dried at 80 °C in vacuo before use. THF was purified by distillation under purified nitrogen atmosphere after being dried by refluxing with sodium benzophenone ketyl before use. Potassium, sodium, and lithium *tert*-butoxides were purified by sublimation under reduced pressure. Sodium *tert*-butoxide and lithium *tert*-butoxide were synthesized from 2-methyl-2-propanol and sodium or lithium metal, respectively. THF solutions of *N*-PMI and alkali-metal *tert*-butoxides were prepared under purified nitrogen before use.

Procedures. The polymerization reaction was carried out in a sealed glass ampule under purified nitrogen atmosphere. After appropriate time intervals polymerization was terminated with hydrochloric acid/methanol and then the reaction mixture was poured into a large amount of an ether/methanol (volume ratio 3/1) mixture. The white precipitate was collected by filtration, washed with ether, methanol, water, and methanol again, and dried at 110 °C in vacuo to constant weight.

Measurements. Vapor pressure osmometry (VPO) was carried out with a Corona 117 vapor pressure osmometer, using THF as solvent. Gel permeation chromatography (GPC) was measured with a Toyo Soda HLC-802A apparatus at 38 °C with TSK gel G4000HXL–G3000HXL–G2000HXL column series, using THF as eluent (flow rate 1.0 mL/min). Molecular weight measured by GPC was calculated from the calibration curve which was corrected[15] by referring to the data of $\bar{M}_w$'s with low-angle light-scattering photometry and of $\bar{M}_n$'s with VPO for four poly(N-PMI) samples with different molecular weights. Low-angle light-scattering photometry was measured with a Toyo Soda LS-8000 light-scattering photometer. ^{1}H NMR was recorded at 279.05 MHz on a JEOL JNM-GX270 at 40 °C using deuteriated dichloromethane as a solvent and dichloromethane as an internal reference. All chemical shifts given in parts per million were transformed to the TMS scale (δ scale) by employing 5.30 ppm as the chemical shift of dichloromethane from TMS. ^{13}C NMR was measured at 67.80 MHz on a JEOL JNM-GX270 at 40 °C under proton decoupling conditions using deuteriated dichloromethane as a solvent and an internal reference. Chemical shifts of each carbon in parts per million were transformed to the TMS scale (δ scale) by employing 53.6 ppm as the chemical shift of the central peak of deuteriated dichloromethane from that of TMS.

Results and Discussion

Reaction Mode of the Polymerization. Figure 1 shows ^{1}H NMR (A) and ^{13}C NMR (B) of poly(*N*-PMI) obtained with lithium *tert*-butoxide as initiator in THF at −72 °C. In Figure 1A the signals observed from 6 to 8 ppm are assigned to phenyl protons. The broad and

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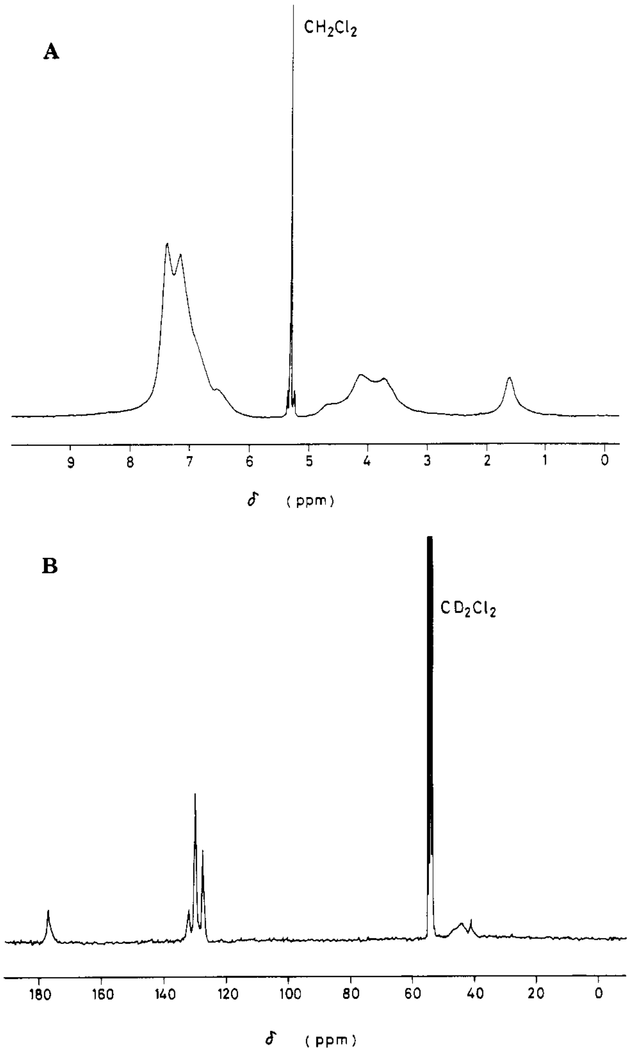

Figure 1. ^1H NMR (A) and ^{13}C NMR (B) of poly(*N*-PMI) obtained with lithium *tert*-butoxide at −72 °C in THF. Measured in CD_2Cl_2.

slightly splitting peaks from 3 to 5 ppm are assignable to methine protons in the polymer main chain. The splitting of the absorption is probably caused by spin–spin coupling and the difference of the configuration of two methine protons (cis or trans) in the five-membered ring of poly(*N*-PMI).

The intensity ratio of phenyl protons to methine protons is observed to be 5:2. The absorption appeared at 1.61 ppm is assignable to the protons of *tert*-butyl group introduced from the initiator at one end of the polymer chain. The signal intensity ratio of this absorption to phenyl protons is in good agreement with the value calculated from the number-average molecular weight of poly(*N*-PMI), assuming one initiator yields one polymer chain. A signal assignable to methylene protons at the other end of the polymer which may be introduced by the termination reaction with an acidic proton is not clearly observed, presumably because of their relatively low concentration, signal broadening, and/or overlapping with the broad methine signal.

Four kinds of carbon signals are observed in ^{13}C NMR (Figure 1B). The signals assigned to carbonyl and phenyl carbons of poly(*N*-PMI) are observed at δ 176.9 and from δ 132.0 to 127.2, respectively. The broadened signal from 40 to 50 ppm is assigned to methine carbons in main chain. The broadening of methine carbons may reflect the difference of configuration or microstructures of poly(*N*-PMI) main chain. The absorption of carbons of *tert*-butyl group is observed at 41.6 ppm. The absorption of the quaternary carbon of the *tert*-butyl group and methylene carbon at the end of the polymer are not detected probably for the same reasons as described above with respect to the terminal methylene group in the ^1H NMR spectrum.

Scheme I

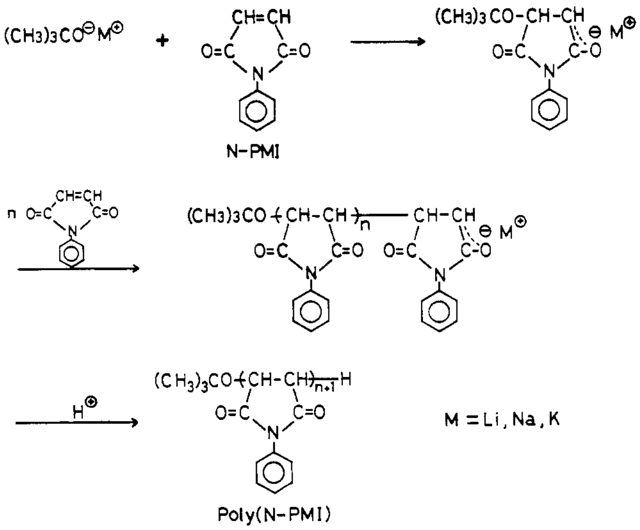

Table I
Anionic Polymerization of *N*-PMI with Alkali-Metal *tert*-Butoxides[a]

tert-butoxide	temp, °C	time, h	conv, %	$\bar{M}_n \times 10^{-3}$ calcd[b]	obsd VPO	obsd ^1H NMR[c]	obsd GPC[d]
Li	−72	192	58	5.0	5.3	5.1	5.1
	0	1.5	89	7.7		7.5	7.9
Na	−72	1.5	100	8.7		8.9	9.1
K	−72	1.5	100	8.7	8.9	9.1	9.3

[a] [*tert*-Butoxide] = 5.6×10^{-3} mol/L, [*N*-PMI] = 2.8×10^{-1} mol/L, in THF. [b] $\bar{M}_n$ = [*N*-PMI]/[*tert*-butoxide] × conv/100 × (mol wt of *N*-PMI). [c] $\bar{M}_n$ obtained by the signal intensity ratio of phenyl group to *tert*-butyl group. [d] $\bar{M}_n$ obtained by GPC with the corrected calibration curve (see Experimental Section).

Similar spectra were obtained for the polymers produced with other alkali-metal *tert*-butoxide initiators. No additional signals except those due to the solvent are observed. These results indicate that polymerization of *N*-PMI with alkali-metal *tert*-butoxides is initiated at carbon–carbon double bonds of *N*-PMI and propagates through opening of the double bonds without any remarkable side reactions such as abstraction of hydrogen at the double bond, carbonyl addition which can be detected in the anionic polymerization of methyl methacrylate, and ring opening of the cyclic imide group; i.e., the anions of initiators and propagating species react exclusively with vinylene group of *N*-PMI (Scheme I). This is probably because the electron density on the carbon–carbon double bond should be strongly reduced by the electron-withdrawing effect of two carbonyl groups and the electrophilicity of carbonyl carbons becomes lower due to the cyclic imide structure.

"Living" Character of Anionic Polymerization of *N*-PMI. Table I shows the results of the anionic polymerization of *N*-PMI with alkali-metal *tert*-butoxides. $\bar{M}_n$'s of poly(*N*-PMI) obtained are in good agreement with those calculated from the initial monomer/initiator ratios and the conversions. These data imply that propagating species of the polymerization systems of *N*-PMI initiated with *tert*-butoxide anions in THF may have a "living" characteristic. Figure 2 shows the relationship between

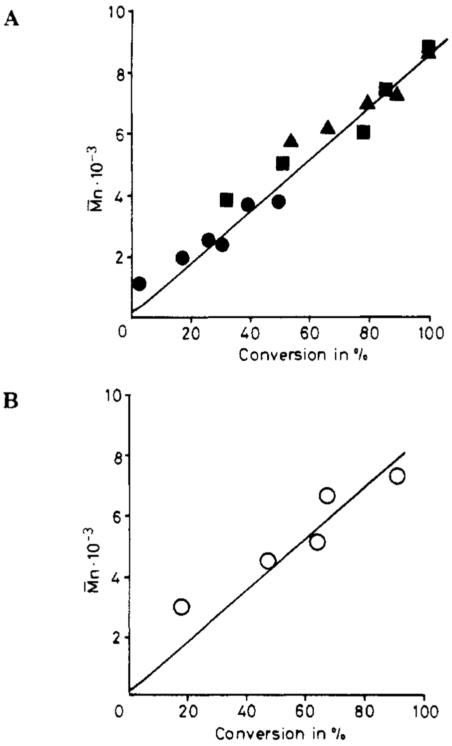

Figure 2. Relationship between conversion of N-PMI and $\bar{M}_n$ of poly(N-PMI). (A) Initiated with lithium *tert*-butoxide (●), sodium *tert*-butoxide (■), and potassium *tert*-butoxide (▲) at −72 °C in THF and (B) lithium *tert*-butoxide at 0 °C in THF.

the conversion of N-PMI and $\bar{M}_n$ of the poly(N-PMI). This figure clearly demonstrates the living character of anionic polymerization of N-PMI with alkali-metal *tert*-butoxide. The molecular weights of the polymers are increased in proportion to the increase of the monomer conversions in the polymerization systems of three kinds of *tert*-butoxides at −72 °C (Figure 2A) and of lithium *tert*-butoxide at 0 °C (Figure 2B). The experimental results are also in good agreement with the theoretical ones expected from the ideal living polymerization system, which is represented by the solid lines in the figure. The slightly upper deviation from the theoretical line of the ideal living polymerization system in the very early stage might be due to rather slow initiation of the polymerization reaction. Although the molecular weight distributions of poly(N-PMI) with lithium *tert*-butoxide are fairly narrow ($\bar{M}_w/\bar{M}_n = 1.26$–$1.36$), these values of polydispersity are not small enough compared with those obtained with the fast initiation polymerization system such as anionic polymerization of styrene initiated with sodium naphthalenide in THF.[16] This may be also caused by the slow initiation of the polymerization.

The living characteristic was also confirmed by a so-called "monomer-addition" experiment in which additional monomer was fed after the first-stage polymerization reaction was completed. The results of monomer-addition experiments are shown in Table II. The monomer added in the second stage is polymerized. $\bar{M}_n$'s of the polymers obtained in the second-stage polymerization are increased and in good agreement with those calculated from the amount of initiator (in moles) and the amount of the monomer consumption in the initial and second stages (in grams). The GPC eluogram of the polymer produced in the monomer addition experiment (Figure 3) clearly demonstrates the increase of the molecular weight after additional monomer is fed.

Table II
Results of Monomer-Addition Experiments in Anionic Polymerization of N-PMI

			initial stage[a]		second stage[b]		
run	*tert*-butoxide	temp, °C	conv of N-PMI, %	$10^{-3}\bar{M}_n$ obsd[c]	conv of N-PMI, %[d]	$10^{-3}\bar{M}_n$ calcd[e]	$10^{-3}\bar{M}_n$ obsd[c]
1	Li	0	100	3.8	50	5.6	5.9
2	Na	−72	100	4.0	50	5.6	6.0
3	K	−72	100	4.0	70	6.3	6.8

[a] [tert-Butoxide] = 5.6×10^{-3} mol/L, [N-PMI] = 1.2×10^{-1} mol/L, polymerization time 3 h, in THF, total volume 10 mL. [b] Amount of added N-PMI is 0.21 g in 10 mL of THF solution (1.2×10^{-1} mol/L solution), polymerization time 1 h. [c] Determined by ^{1}H NMR. [d] Based on the amount of newly added N-PMI. [e] Calcd $\bar{M}_n$ = (amount of polymerized N-PMI in g) × (mol wt of *tert*-butoxide)/(amount of *tert*-butoxide in g).

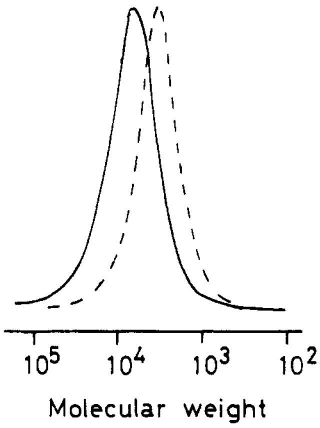

Figure 3. Molecular weight distributions of poly(N-PMI) produced in the first stage (- - -) and the second stage (—) of the monomer addition experiment initiated with lithium *tert*-butoxide (see Table II, run 1).

It may be concluded that the anionic polymerization of N-PMI initiated with alkali-metal *tert*-butoxide anion in THF takes place only at the carbon–carbon double bond and propagates in the living polymerization mechanism without appreciable termination and chain-transfer reactions, although the monomer possesses carbonyl groups.

Acknowledgment. We thank Dr. Y. Tezuka (The Technological University of Nagaoka) for measurements and analyses of ^{1}H NMR and ^{13}C NMR spectra.

Registry No. Poly(N-PMI), 25101-57-9; N-PMI, 941-69-5; LiOBu-t, 1907-33-1; NaOBu-t, 865-48-5; KOBu-t, 865-47-4.

References and Notes

(1) Tsuruta, T. In *Progress in Polymer Science, Japan*; Okamura, S., Takayanagi, M., Eds.; Kodansha: Tokyo, 1972; Vol. 3, pp 1–47.
(2) Yuki, H.; Hatada, K. *Adv. Polym. Sci.* **1979**, *31*, 1.
(3) Lyons, A. R. *J. Polym. Sci., Part D* **1972**, *6*, 251.
(4) Schildknecht, C. E. *Ind. Eng. Chem.* **1958**, *50*, 107.
(5) Hopff, H.; Lussi, H.; Allison, A. *Makromol. Chem.* **1960**, *44/46*, 95.
(6) Gilbert, H.; Miller, F. F.; Averill, S. J.; Schmidt, R. F.; Tsewart, F. D.; Trumbull, H. L. *J. Am. Chem. Soc.* **1954**, *76*, 1074.
(7) Cubbon, R. C. P. *Polymer* **1965**, *6*, 419.
(8) Yamada, M.; Takase, I.; Kobayashi, M. *Kobunshi Kagaku* **1972**, *29*, 144.
(9) Oishi, T.; Ishikawa, T.; Kimura, T. *Kobunshi Ronbunshu* **1979**, *36*, 751.
(10) Otsu, T.; Yamada, T.; Shiraishi, K.; Mori, S. *Polym. Bull. (Berlin)* **1984**, *12*, 449.
(11) Hagiwara, T.; Mizota, J.; Hamana, H.; Narita, T. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 169.
(12) Hagiwara, T.; Someno, T.; Hamana, H.; Narita, T. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1011.
(13) Hagiwara, T.; Takeda, M.; Hamana, H.; Narita, T. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 167.
(14) Hagiwara, T.; Sato, J.; Hamana, H.; Narita, T. *Makromol. Chem.* **1987**, *188*, 1825.

(15) Balke, S. T.; Hamielec, A. E.; Leclair, B. D.; Pearce, S. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1969**, *8*, 54.
(16) Geacintov, C.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1962**, *84*, 2508.

Modification of the Avrami Treatment of Crystallization To Account for Nucleus and Interface

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Introduction and Review of the Avrami Treatment

The kinetics of crystallization of polymers is often fitted to the Avrami treatment.[1] Identical treatments were proposed earlier than the one by Avrami,[2] by Kolmogoroff[3] and Johnson and Mehl[4], and later, by Evans.[5] All can be related to the problem of impinging waves, first solved by Poisson.[6] The solution can be briefly stated for the case of three dimensions by saying that the probability of a point not to be overrun by expanding spheres, $P_o(t)$, is equal to $\exp(-E)$, where E is the expectation volume fraction for interpenetrating spheres expanding unhindered by impingement. The value of E increases from zero at time zero without limit to values beyond one as time increases.

For the application to crystallization of macromolecules, a number of specific modifications are usually made. First, nucleation is assumed to lead to negligible amounts of crystal formation and is either athermal (i.e., all N nuclei per unit volume are preformed and active at time zero) or thermal (i.e., the number of nuclei in the uncrystallized volume increases as a function of time $N(t) = at$). Second, the linear crystal growth rate, v, is assumed to be constant from nucleation to impingement, and the impingement leads to a negligible volume fraction of interface. These two assumptions lead to the following expectation volume fraction (also called the free growth approximation of the crystallization kinetics)

$$E = 4\pi N v^3 t^3/3 \tag{1}$$

for athermal nucleation,[1] and

$$E = \pi a v^3 t^4/3 \tag{2}$$

for thermal nucleation.[1] The corresponding Avrami equation is usually cast in the form

$$1 - v^c = \exp[-Kt^n] \tag{3}$$

where $1 - v^c$ is the volume fraction of polymer outside the spherically expanding crystal, K is the collection of constants that can be evaluated by comparison with eq 1 and 2, and n is the "Avrami exponent", in the present cases 3 and 4, respectively. In this paper, both assumptions will be modified to account for a crystallization that approaches the case of "cold crystallization",[7,8] a case of crystallization from a highly viscous state that permits only minimum rearrangement of the crystallizable units. A similar model of crystallization has been proposed as an "Erstarrungsmodell"[9] and has also been fitted to the computation of the statistics of crystallization of macromolecular anisotropic melts.[10]

Further assumptions that are implied in the use of eq 3 for the description of crystallization of macromolecules are an isometric crystal morphology so that the probability $P_o(t)$ does not depend on direction from the nearest nucleus. The spherulitic crystal superstructure often seen in macromolecules[11] ideally fulfills this condition but needs a special correction for partial crystallization within the spherulite boundaries, usually effected by normalizing the crystallinity at infinite crystallization-time to one. A frequent complication is continuing an approach to crystalline perfection within the spherulite. It has been corrected for the case of slow rates by additional term in eq 3.[1] Additional complications such as those due to volume change on crystallization, different crystal geometries, and different crystal branching have been described in detail and can be added to the modification proposed here when necessary.

All of these modifications have led to Avrami exponents of one or larger. Recent experiments have, however, shown an increasing number of cases of very small Avrami exponents,[12-14] in some cases even approaching zero. It will be shown in this paper that these low exponents could find an explanation in large nuclei numbers followed by rather limited growth slowed down by the production of rigid amorphous portions[15-19] between the microphase-separated crystals (soft impingement, see below).

Crystallization with Nonnegligible Volume Fraction of Nuclei

Usually, one does not take the volume fraction of nuclei into account since it is often very small and less than 1% of the total crystallinity in a polymeric system. However, when the volume fraction of nuclei increases up to 10% or more, the influence of such a large volume fraction of nuclei to overall crystallization becomes obvious.

Recent observations of the kinetics involving condis crystals show that a nonnegligible volume fraction of nuclei does exist and plays an important role in their overall crystallization behavior. For example, in the cases of thermotropic copolyesters produced by Celanese [with different 1,4-hydroxybenzoic acid (HBA) and 2,6-hydroxynaphthoic acid (HNA) compositions], a fast solidification process can be found within seconds during quenching the materials from their anisotropic melts. About 0.5–0.8 kJ/mol of heats of transition is formed. This corresponds to at least 5–10% or more of the total (condis) crystallinity.[12,20,21] It is also found that these earlier grown crystals grow slowly at later times and hamper further crystal growth under isothermal conditions.[12] It indicates that the earlier crystals as nuclei of further growth are being exhausted, and the number of active nuclei decrease with increasing time. Assuming that such a decrease can be cast in the form

$$N(t) = N_o t^a \tag{4}$$

where a is negative [$a = 0$ if a constant number of nuclei (athermal) are considered], the Avrami equation (eq 3) can now be written as

$$\log\,[-(\ln\,(1 - v^c))] = \log g + \log N_o + n \log v + (n + a) \log t$$

$$\log\,[-(\ln\,(1 - v^c))] = \log K_1{}^* + (n + a) \log t \tag{5}$$

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