# Effect of the Molecular Structure of the Polymer and Nucleation on the Optical Properties of Polypropylene Homo- and Copolymers

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$$\ln H_{red} = \lambda \ln T_{red}$$
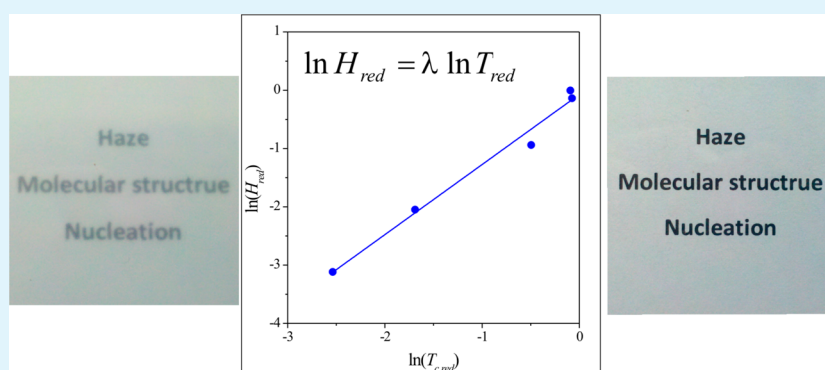
ABSTRACT: Two soluble nucleating agents were used to modify the optical properties of nine PP homo- and random copolymers. The ethylene content of the polymers changed between 0 and 5.3 wt %. Chain regularity was characterized by the stepwise isothermal segregation technique (SIST), while optical properties by the measurement of the haze of injection molded samples. Crystallization and melting characteristics were determined by differential scanning calorimetry (DSC). The analysis of the results proved that lamella thickness and change in crystallinity influence haze only slightly. A model was introduced which describes quantitatively the dependence of nucleation efficiency and haze on the concentration of the nucleating agent. The model assumes that the same factors influence the peak temperature of crystallization and optical properties. The analysis of the results proved that the assumption is valid under the same crystallization conditions. The parameters of the model depend on the molecular architecture of the polymer. Chain regularity determines supermolecular structure and thus the dependence of optical properties on nucleation.

KEYWORDS: polypropylene, crystalline structure, nucleation, haze, molecular structure

1. INTRODUCTION

Transparency and optical clarity are basic requirements for a number of products, and the demand for them increases continuously. Amorphous polymers, for example, PVC, PC, PS, and PMMA, were used in such areas earlier, since in semicrystalline polymers light scattered on different structural units makes the products opaque. In polyolefins, incident light is scattered on the crystallites, spherulites, and also on the interface between the amorphous and crystalline phases having different refractive indices.[1] Crystalline units are often large enough to interfere with visible light and this interference results in considerable haze that is often used for the characterization of the appearance of a plastic product. Haze is the total flux of light scattered within the angular range between 2.5 and 90° and normalized to the total transmitted flux.[1]

Lately considerable effort has been focused on the improvement of the optical properties of polymers including PP. Earlier Bheda and Spruiell[2] as well as White and Doun[3] carried out extensive experiments to determine correlations between the type of the polymer, nucleating agent content, processing conditions, and the optical properties of polymer products. They found that both polymer properties, including melt flow rate (MFR), and processing conditions strongly influence transparency and other optical characteristics.

Recently the use of polypropylene for the production of transparent products became industrial practice due to the low haze achieved and the acceptable price of this polymer.[4] Low haze materials are usually prepared from random copolymers

and optical properties are improved further by the use of clarifiers based on different sorbitol derivatives.[5−9] These latter additives dissolve in the polymer generating a microcrystalline structure and improve haze considerably.[10,11] In the past decade, a relatively new family of nucleating agents based on trisamide derivatives appeared as the competitor of sorbitol clarifiers.[12−15] However, the efficiency of the clarifier depends very much also on the characteristics of the polymer used and on processing conditions, as mentioned above. Quite a few papers are dealing with the effect of clarifiers on the optical properties of PP,[10,16−18] but according to our literature survey very few relates the achieved characteristics to the structure of the polymer.[19] The selection of the polymer used usually occurs on trial and error bases.

The goal of the study reported here was to find correlations between the molecular structure of polypropylene homo- and random copolymers and the optical properties of products prepared from them. Two different soluble clarifiers were used for the modification of optical properties, a sorbitol type additive and the recently developed and marketed trisamide product of BASF.[12] Haze was used for the characterization of optical properties and it was related to various aspects of crystalline structure. A model was introduced to describe correlations quantitatively and relate optical properties to the molecular structure of the polymers studied, if such correlation existed at all.

2. EXPERIMENTAL SECTION

Nine different polypropylene samples were used in the study: two PP homopolymers and seven random copolymers. All were supplied by Borealis Polyolefine GmbH. The melt flow rate (ISO 1133, 230 °C, 2.16 kg) of the polymers changed in a wide range between 1.5 and 15 g/10 min, while their ethylene content varied between 0 and 5.3 wt %. The characteristics of the polymers used are compiled in Table 1. Polymers are identified according to their composition.

Table 1. Molecular Characteristics of the Polymers Used in the Study

polymer	Et content (wt %)[a]	isotactic run length (monomer unit)[b]	M_w (kg/mol)[c]	M_w/M_n	MFR (g/10 min)
H1	0	47.2	232	3.4	2.0
H2	0	51.8	223	4.7	12.0
R17	1.7	33.9	211	2.7	8.0
R21	2.1	41.0	217	5.4	14.0
R27	2.7	50.3	195	4.5	15.0
R28	2.8	36.0	203	4.6	12.0
R35	3.5	33.6	244	3.6	2.0
R42	4.2	32.1	317	3.7	1.5
R53	5.3	29.4	195	3.2	12.0

[a]Ethylene content. [b]Determined by SIST. [c]Weight-average molecular mass.

H1 and H2 indicates the two homopolymers used, while the abbreviation of random copolymers contains ten times their ethylene content. Accordingly, R21 was prepared with 2.1 wt % ethylene as comonomer. Molecular architecture, that is, the regularity of the chains, was characterized by the stepwise isothermal segregation technique (SIST).[20] Under chain regularity, we understand isotactic run length, that is, the average length of the chain that contains isotactic monomer units. Isotactic run length is limited both by the number of comonomer units and stereodefects, and it determines maximum lamella thickness, which can develop in the polymer. The SIST experiments were carried out using a PerkinElmer DSC 7

apparatus between 160 and 100 °C. After the elimination of thermal and mechanical prehistory at 220 °C for 5 min, the samples were cooled to 160 °C at a rate of 80 °C/min and held there for 3 h. Subsequently, the samples were cooled to the next crystallization temperature (150 °C) and kept there for another 3 h. Each temperature ramp took 3 h, and each step was 10 °C. After the final crystallization step at 100 °C, the samples were reheated again at a rate of 10 °C/min and melting traces were recorded. Optical properties were modified by nucleation. Two soluble clarifiers were added to the polymers in different amounts according to their solubility. 1,2,3-desoxy-4,6;5,7-bis(4-propylbenzylidene)nonitol, a sorbitol type clarifier (Millad NX 8000, Milliken), was applied at 0, 1000, 2000, 3000, 4000, and 5000 ppm, while trisubstituted 1,3,5-benzene-trisamide compound[15,21] (XT 386, BASF, Germany), was added at 0, 50, 100, 150, 200, and 500 ppm to the polymers.

The stabilizers and the nucleating agents were homogenized with the polymer in a Henschel FM/A10 high speed mixer at 700 rpm for 5 min. The blend was melt compounded in a Brabender DSK 42/7 twin screw compounder at 50 rpm and 200, 220, 230, 230 °C set temperatures. The compound was injection molded to 1 mm thick plaques using a Demag IntElect 50/330-100 machine at 200−210−220−230 °C zone and 40 °C mold temperatures. Injection rate was 20 mm/s, holding pressure 500 bar, and holding time 15 s.

The melting and crystallization characteristics of the samples were determined by differential scanning calorimetry (DSC) using a PerkinElmer DSC 7 equipment. Samples of 3−5 mg were heated to 220 °C at 10 °C/min heating rate, kept there for 5 min to erase thermal history, and then cooled down to 50 °C with the same rate to record crystallization characteristics. After 1 min holding time, the samples were heated again to 200 °C at 10 °C/min heating rate to determine melting temperature and the heat of fusion. The distribution and average thickness of the lamellae were calculated from the second heating run.[22] The optical behavior of the polymers was characterized by haze measurements carried out on the 1 mm thick injection molded plates.

3. RESULTS AND DISCUSSION

The results are discussed in several sections. First we show the effect of nucleation on the properties of the polypropylenes selected, and then discuss the relation of crystalline structure and optical characteristics. After the quantitative analysis of these correlations an attempt is made to relate the determined parameters to the molecular structure of the polymer.

3.1. Nucleation and Properties. Nucleation is very often used in polypropylene to increase stiffness and strength,[23−29] to improve productivity by increasing the temperature of crystallization[27−30] and to modify optical properties.[17,18,31] The efficiency of nucleation is usually estimated by DSC measurements, by changes in the peak temperature of crystallization (T_{cp}),[32] which can be related to the thickness of the lamellae formed.[33] DSC traces offer information about crystallinity as well. The effect of the amount of the sorbitol type nucleating agent on the crystallization characteristics of two selected polymers is presented in Figure 1.

In accordance with experience, a stepwise increase in crystallization temperature is observed due to the solubility of the clarifier; efficient nucleation occurs only above the solubility limit.[6,31,34] The influence of solubility is more pronounced in the homopolymer (H2) than in the random copolymer (R35) presented in the figure. Different effect and efficiency of nucleation can be observed also in the changes of crystallinity. The ordered crystalline fraction of the homopolymer clearly increases upon nucleation, while that of the random copolymer practically does not change. The relations presented in Figure 1 are generally valid for all the PP polymers studied.
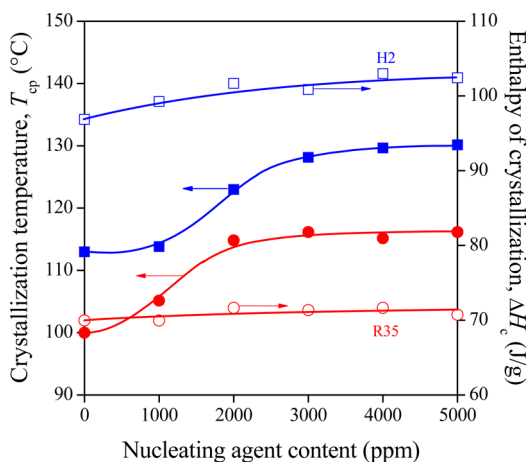
Figure 1. Crystallization characteristics of PP polymers plotted against the amount of sorbitol clarifier. Effect of polymer characteristics. Symbols: (○, ●) random copolymer (R35), (□, ■) homopolymer (H2), (○, □) enthalpy of crystallization, and (●, ■) peak temperature of crystallization.

The effect of nucleation on the haze of the same polymers is shown in Figure 2. A much larger decrease in haze occurs in the
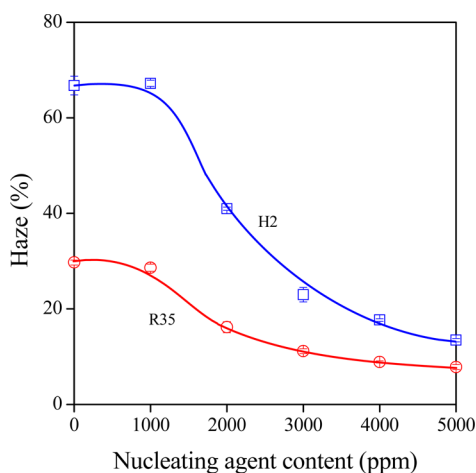

Figure 2. Effect of nucleation on the haze of the polymers of Figure 1. Symbols: (○) random copolymer, (□) homopolymer; nucleating agent: sorbitol.

H2 homopolymer than in the R35 random copolymer, but the minimum haze achieved is smaller in the latter. The haze value of a "clear" product must be below 10%; thus, the figure amply demonstrates the reason for using random copolymers for clarified products. The solubility of the clarifier has the same effect on haze as on crystallization characteristics.

Figures 1 and 2 also prove that both the efficiency of nucleation and the actual values of the different characteristics depend on the molecular structure of the polymer. The absence of a comonomer results in much larger crystallinity, a larger increase in the peak temperature of crystallization and a significantly larger improvement in haze in the homopolymer than in the random copolymer. Nevertheless, this latter is more advantageous for the purpose discussed in this paper as smaller haze values can be achieved with them. Since all properties depend on the molecular structure of the polymer, we may hope that the wide range of characteristics covered by the

studied polymers (see Table 1) will allow us to establish correlations between molecular structure and optical properties.

3.2. Crystalline Structure and Optical Properties. The properties of crystalline polymers are determined by their structure, that is, by crystal modification, crystallinity, lamella thickness, spherulite size, and the number of tie molecules. Modulus was shown to depend on crystallinity and lamella thickness,[25] while fracture resistance mainly on the latter characteristic.[35−38] All the polymers studied crystallize in the α-modification, and the number of tie molecules probably does not influence optical properties much. On the other hand, crystallinity, spherulite size, lamella thickness, and probably also the interface area between the crystalline and amorphous phases may play a role in the determination of haze. Since this latter must be closely related or even proportional to lamella thickness, we do not consider it separately in the further course of the analysis.

Figure 3 shows the correlation of haze and lamella thickness for five of the polymers studied. Lamella thicknesses were
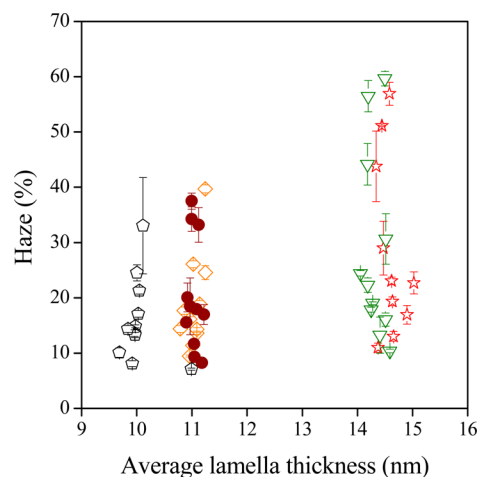

Figure 3. Independence of haze of the average lamella thickness of PP random copolymers. Symbols: (⬠) R53, (●) R17, (◇) R42, (☆) R21, and (▽) R27.

derived from melting traces recorded in the DSC cell as described by Romankievicz and Sterzynski.[22] The results clearly prove that no correlation whatsoever exists between the average lamella thickness of the polymers containing different type and amount of nucleating agents and their haze irrespective of ethylene content as well as other characteristics of molecular structure. This is more or less understandable since average lamellae thicknesses are below 20−30 nm and considerable light scattering starts above this range. Obviously, lamella thickness does not influence haze, which is further supported by the fact that haze decreases with increasing amount of the clarifiers, while lamella thickness increases at the same time. This conclusion is in accordance with our previous results showing the independence of optical properties of lamella thickness and their dependence on nucleus density.[31] Plotting haze against crystallinity resulted in very similar correlations as in Figure 3 and indicated the almost complete independence of the two characteristics, that is, haze and crystallinity (not shown). Moreover, crystallinity remains constant or also increases upon nucleation, while haze changes in the opposite direction. This controversial effect indicates clearly that

improvement in crystallinity has a minor effect, but changing in morphology affects haze predominantly.

Haze is plotted as a function of the peak temperature of crystallization in Figure 4. A clear correlation can be established
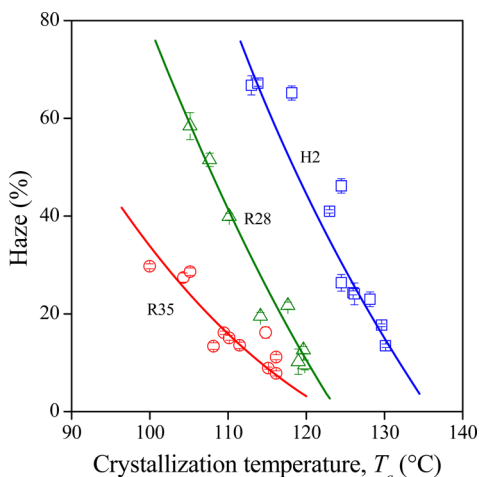

Figure 4. Effect of haze on the peak temperature of crystallization for three of the PP polymers studied. Symbols: (○) R35, (△) R28, and (□) H2.

for all polymers studied; that is, haze decreases with increasing nucleating effect. As mentioned above, nucleation changes several factors of crystalline structure; it increases crystallinity, lamella thickness, and nucleus density, and decreases the size of the spherulites. In the case of soluble clarifiers, spherulites might not even form; often a network structure and a microcrystalline structure have been observed in their presence.[10,11,31] We may conclude from these results that the main factor determining haze is the size of the supermolecular units formed during the crystallization of our polymers, and they decrease with increasing amount of nucleating agent. This conclusion agrees well with the analysis of Haudin[39] claiming a quantitative correlation between the intensity of scattered light and the size of the spherulites. Although processing conditions, especially cooling rate, influence supermolecular structure (nucleus density and spherulite size) and consequently haze,[40,41] all samples were prepared and experiments carried out under the same conditions thus we do not consider and discuss crystallization kinetics in the subsequent analysis.

3.3. Model, Quantitative Analysis. According to Figures 1 and 2, both crystallization characteristics and optical properties depend strongly on the concentration of the nucleating agent added (c). We may assume that both the temperature of crystallization (T_c) and haze (H) depend on this variable through a common $f(c)$ function, that is,

$$\frac{\partial T_c}{\partial c} \sim f(c) \quad \text{and} \quad \frac{\partial H}{\partial c} \sim f(c) \tag{1}$$

The results clearly show that the $T_c(c)$ function increases monotonously and reaches a saturation value, $T_{c\infty}$, in the studied range, which corresponds to industrially relevant concentrations, while the $H(c)$ function decreases simultaneously to reach a minimum value, H_∞. Since at large nucleating agent content the $T_c(c)$ function practically does not change, thus at $T_c \rightarrow T_\infty$ the differential $\partial T_c/\partial c \rightarrow 0$. As a consequence, eq 1 must be modified to obtain

$$\frac{\partial T_c}{\partial c} = \beta(T_{c\infty} - T_c)f(c), \quad (T_{c\infty} - T_c) \geq 0 \text{ and } \beta \geq 0 \tag{2}$$

and for haze

$$\frac{\partial H}{\partial c} = -\alpha(H - H_\infty)f(c), \quad (H - H_\infty) \geq 0, \quad \text{and}$$

$$\alpha \geq 0 \tag{3}$$

Instead of the $(T_{c\infty} - T_c)$ and $(H - H_\infty)$ differences, we may use any $s(T_{c\infty} - T_c)$ and $p(H - H_\infty)$ function which satisfies the condition that $s(T_{c\infty} - T_c) = 0$ and $p(H - H_\infty) = 0$ if $T_{c\infty} = T_c$ and $H = H_\infty$. We may assume that the $f(c)$ function is proportional to some positive power of the concentration, and then eqs 2 and 3 take the following form

$$\frac{\partial T_c}{\partial c} = \beta(T_{c\infty} - T_c)c^n, \quad n > 0, \quad (T_{c\infty} - T_c) \geq 0,$$

$$\text{and} \quad \beta \geq 0 \tag{4}$$

$$\frac{\partial H}{\partial c} = -\alpha(H - H_\infty)c^m, \quad m > 0, \quad (H - H_\infty) \geq 0,$$

$$\text{and} \quad \alpha \geq 0 \tag{5}$$

Integrating the equations and using the initial conditions that $T_c(c = 0) = T_{c0}$ and $H(c = 0) = H_0$, we obtain the final correlations for the composition dependence of the temperature of crystallization and haze, respectively

$$T_c = T_{c\infty} + (T_{c\infty} - T_0) \exp\left(-\frac{\beta c^{n+1}}{n+1}\right) \tag{6}$$

$$H = H_\infty + (H_0 - H_\infty) \exp\left(-\frac{\alpha c^{m+1}}{m+1}\right) \tag{7}$$

The validity of the approach can be checked in several ways. We can fit eqs 6 and 7 to the respective T_c and H values and see the agreement or disagreement of the measured data and the fitted function. Such correlations are presented in Figure 5 for T_c and in Figure 6 for haze in the case of the R21 polymer. The agreement between the measured and calculated values is quite good. Very good fits were obtained for practically all the
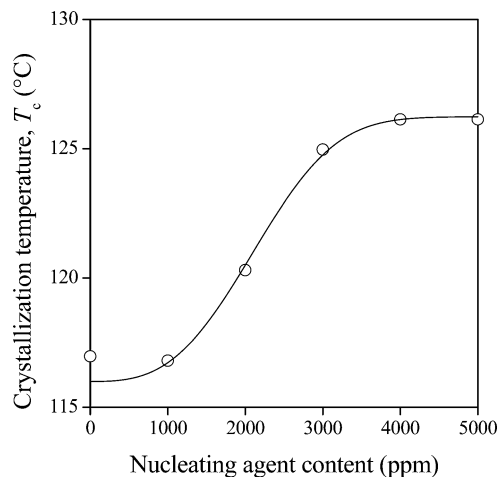

Figure 5. Fitting of eq 6 to crystallization temperatures determined for the R21 polymer as a function of nucleating agent content (sorbitol type nucleating agent).
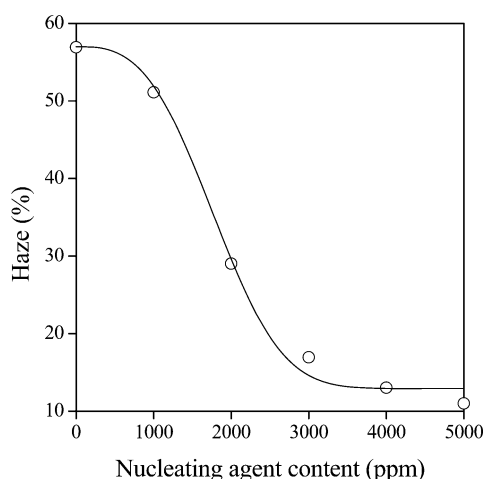
Figure 6. Quantitative description of the composition dependence of haze for the R21 polymer (sorbitol type nucleating agent).

The approach and the model are acceptable if we obtain a straight line by plotting the two variables of eq 12 against each other in logarithmic scale. The correlation is presented for the R21 polymer in Figure 7. Although a very good linear
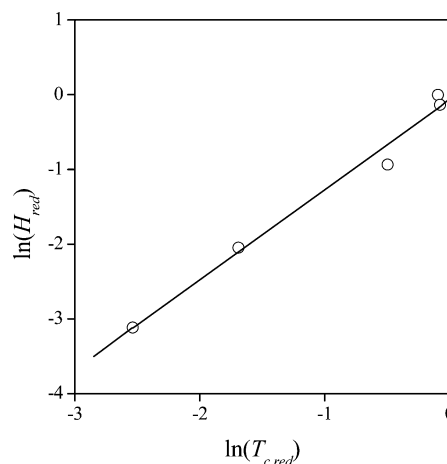

Figure 7. Reduced haze plotted against reduced temperature of crystallization according to eq 12.

materials nucleated with the sorbitol clarifier, while more difficulties were encountered during the fitting of data obtained on materials prepared with the trisamide compound. The small concentrations used and homogenization problems may account for the larger scatter of the points and thus for problems in using the model. In the cases presented in Figures 5 and 6, we obtained the same value, 1.98, for the power law constant of n and m, indicating that the same factors influence both crystallization characteristics and haze. Unfortunately, the agreement between the parameters determined from the concentration dependence of crystallization temperature (n) and haze (m) is not as good for all the polymers studied because of the reasons mentioned above. The homogeneity of the samples, the standard deviation of the measurements, and the error of fitting, especially at values close to saturation, all may contribute to the deviations.

We can also check the validity of the approach by deriving a direct correlation between haze and the peak temperature of crystallization. We can do that if we divide eq 3 with eq 4. Using the equality

$$\frac{\partial H}{\partial c}\left(\frac{\partial T_c}{\partial c}\right)^{-1} = \frac{\partial H}{\partial c}\frac{\partial c}{\partial T_c} = \frac{\partial H}{\partial T_c} \tag{8}$$

we can eliminate the concentration of the nucleating agent as variable and obtain the following correlation

$$\frac{\partial H}{\partial T_c} = \lambda \frac{H - H_\infty}{T_{c\infty} - T_c} \quad \text{where} \quad \lambda = \frac{\alpha}{\beta} \tag{9}$$

Integration of eq 9 leads to the solution

$$(H - H_\infty) = C(T_{c\infty} - T_c)^\lambda \tag{10}$$

Constant C can be derived from the initial conditions used before and we obtain the final solution

$$\frac{H - H_\infty}{H_0 - H_\infty} = \left(\frac{T_{c\infty} - T_c}{T_{c\infty} - T_{c0}}\right)^\lambda \tag{11}$$

which can be written in a simplified form, if we introduce reduced variables

$$\ln H_{red} = \lambda \ln T_{red} \tag{12}$$

correlation was obtained for the R21 polymer, the agreement with theory is not always so good, mainly for values close to $T_{c\infty}$ and H_∞ for reasons discussed above.

The relative values of the parameters characterizing solubility (n, m) and the effect of nucleation (rate of property change, β, α) are plotted against each other in Figure 8. The plot offers

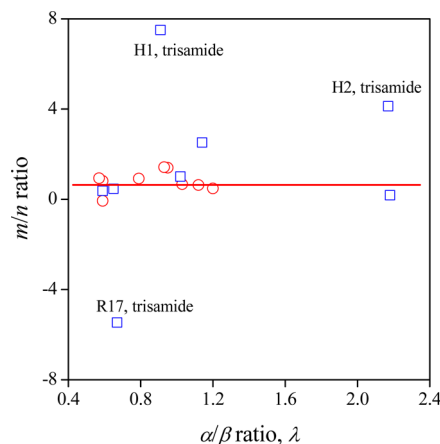**Figure 8.** Relative values of the parameters characterizing solubility (n, m) and the rate of property change on nucleation (β, α) plotted against each other.

further information about the validity of the approach, but also about the reliability of the measurements. Most of the m/n values are very similar, around 1 indicating that the model can be applied for the analysis of nucleation and haze and that crystallization characteristics and optical properties are closely related indeed. λ covers a much wider range, probably because of the very small value of the parameters α and β, which are influenced by experimental error much more than the power law constants. Three points deviate strongly from the general tendency all belonging to materials containing the trisamide nucleating agent. This additive is used in very small amounts and experience shows that it is very difficult to homogenize

properly. Solubility also might depend on factors not controlled adequately during processing. In spite of uncertainties and deviations from the general tendency we can use the approach for the analysis of the effect of molecular structure on nucleation and on the optical properties of nucleated PP samples.

3.4. Molecular Structure and Haze. The molecular structure of polypropylene random copolymers depends very much on the catalyst and the technology used for polymerization. Ethylene content and chain regularity are used the most often for the characterization of copolymers in industrial practice; the latter can be determined by NMR or SIST measurements. The two quantities, that is, ethylene content and regularity determined by SIST, are plotted against each other in Figure 9. A relatively close correlation is obtained for
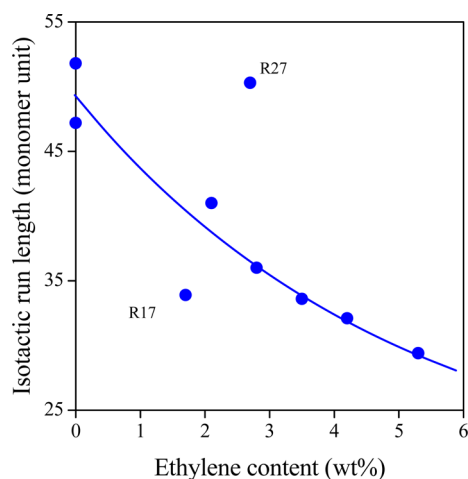
Figure 9. Correlation between the quantities characterizing the composition (ethylene content) and chain structure (regularity, SIST) of the polymers studied.

the polymers used in the study with two deviating points. These two are experimental products with similar ethylene content (1.7 and 2.7 wt %, respectively), but considerably differing chain regularity. The correlation indicates that ethylene content is a major factor determining the molecular architecture of PP random copolymers,[42] but not the only one and other factor or factors also play a role.

We plotted all parameters derived from the model (H_0, H_∞, T_{c0}, $T_{c\infty}$, α, β, n, m, λ) against quantities characterizing molecular structure, that is, ethylene content and chain regularity (SIST), but also against each other. We refrain from presenting them all and show only a few correlations demonstrating the relationships between the efficiency of nucleation and optical properties of PP homo- and copolymers and their molecular structure. Figure 10 supplies further proof for our assumption that both crystallization temperature and haze can be described by the same correlation. Saturation values of T_c and H are plotted against each other in the figure, and we obtain a reasonably close correlation proving that both characteristics depend on the same factors.

The effect of chain regularity on the saturation value of crystallization temperature is presented in Figure 11. The correlation is reasonable especially for the polymers containing the sorbitol clarifier (○). Much larger deviations can be observed from the general tendency for polymers containing the XT nucleating agent (□) probably for reasons discussed in
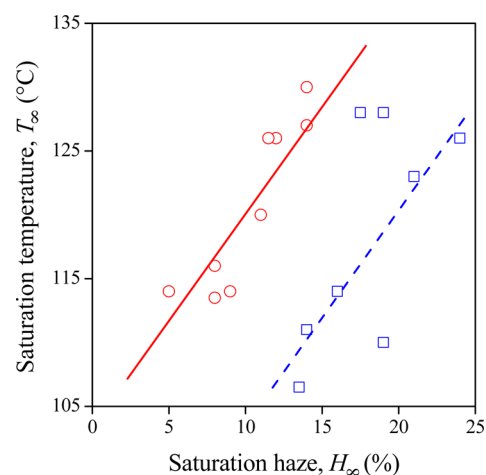
Figure 10. Correlation between the saturation values of crystallization temperature and haze derived from the model. Symbols: (○) sorbitol, (□) trisamide.
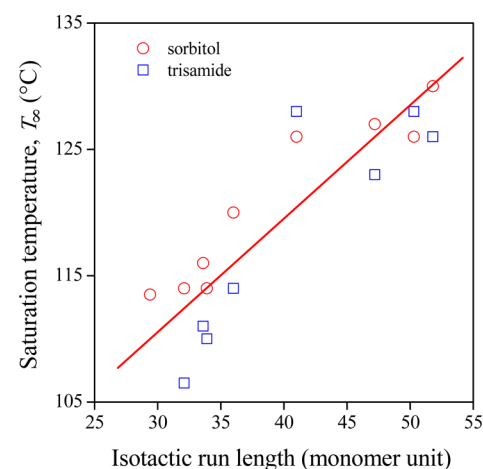
Figure 11. Effect of chain regularity on the saturation temperature of crystallization. Symbols: (○) sorbitol, (□) trisamide.

the previous section. The dissimilar effect and behavior of this nucleating agent from that of the sorbitol is clearly shown also by Figure 12 in which H_∞ values are plotted against chain
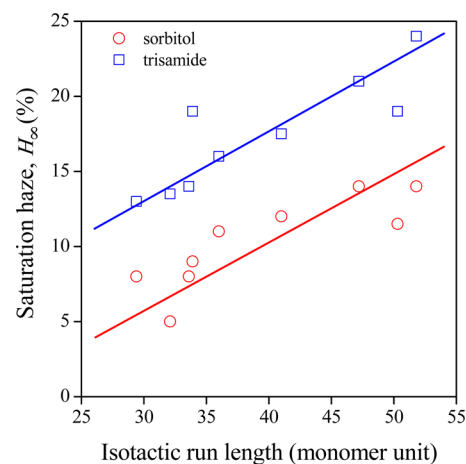
Figure 12. Correlation between haze saturation values and chain regularity. Symbols: (○) sorbitol, (□) trisamide.

regularity. Rather surprisingly we obtain two correlations instead of one running more or less parallel to each other. The results also indicate that the sorbitol clarifier improves clarity more efficiently than the other nucleating agent used. Moreover, this difference cannot be explained with imperfect homogenization or the inadequacy of the model, since the correlations are clear for both additives. The relation of the parameters derived from the model is less close to ethylene content proving our earlier conclusion that chain regularity is closely related to ethylene content, but depends also on other factors (see Figure 8). We must also mention here that the initial values of crystallization temperature (T_{c0}) and haze (H_0) depend similarly on chain regularity as the saturation values indicating that the characteristics of the polymer play a determining role in nucleation, but also in the final haze value which can be achieved with them.

4. CONCLUSIONS

The analysis of the effect of two soluble clarifiers on the optical properties of nine PP homo- and random copolymers proved that lamella thickness and improvement in crystallinity influence haze only slightly. A model was introduced which describes quantitatively the dependence of nucleation efficiency and haze on the concentration of the nucleating agent. The model assumes that the same factors influence the peak temperature of crystallization and optical properties. The analysis of the results proved the assumption valid and also showed that the size of the supermolecular units is the main factor determining optical properties. The parameters of the model depend on the molecular architecture of the polymer. Chain regularity determines supermolecular structure and thus the dependence of optical properties on nucleation.

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Notes
The authors declare no competing financial interest.

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