

Crystallization of Poly(ethylene terephthalate) Modified with Codiols

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ABSTRACT: The nucleation of poly(ethylene terephthalate) (PET) by codiols and olefinic segments was studied. The codiols 1,5-pentanediol, 1,8-octanediol, 2,5-hexanediol, and 1,3-dihydroxymethyl benzene were copolymerized into PET in a concentration range of 0–10 mol %. The melting (T_m), crystallization (T_c), and glass-transition (T_g) temperatures were studied. These codiols were found to be able to nucleate PET at low concentrations, probably by lowering the surface free energy of the chain fold. However, the codiols also disturbed the structural order of the polymer, resulting in a decrease in both the T_m and T_c values. The optimum codiol concentration was found to be at around 1 mol %, which is lower than previously reported. A diamide segment *N,N'*-bis(*p*-carboxymethoxybenzoyl)ethanediamine (T2T) was found to be a more effective nucleator than the codiols; however, no synergy was observed between the nucleating effect of the diamide segment T2T and that of the codiol. An olefinic diol (C_{36} -diol) with a molecular weight of 540 g/mol was also copolymerized into PET in a concentration range of 0–21 wt %. Only one T_g was observed in the resulting copolymers, suggesting that the amorphous phases of PET and the C_{36} -diol are miscible. The main effect of incorporating the C_{36} -diol into PET was the lowering of the T_g ; thus, the C_{36} -diol is an internal plastifier for PET. The C_{36} -diol had little effect on the T_m value; however, the T_c value actually increased in the 11.5 wt % copolymer. As the T_g decreased and the T_c increased, the crystallization window also increased and thereby the likelihood of crystallization. Therefore, the thermally stable C_{36} -diol appears to be an interesting compound that may be useful in improving the crystallization of PET. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2676–2682, 2001

Key words: poly(ethylene terephthalate); crystallization; codiols; C_{36} -diol; copolymers

INTRODUCTION

Poly(ethylene terephthalate) (PET) is the most important polyester. In comparison with poly(butylene terephthalate) (PBT), PET generally

exhibits better properties in that it has a higher dimensional stability, modulus, and yield stress, but a lower impact strength. Its major drawback is the slow rate of crystallization. When used as an engineering plastic, PET is processed by injection molding. For the success of this process, it is important that the PET crystallizes rapidly and that the crystallization is complete. There are a number of ways to increase the rate of crystallization of PET, including heterogeneous nucleation (talc),^{1,2} codiols at low concentrations (5 mol %),³ long diols

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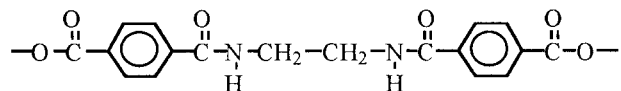
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(polyethers),^{4,5} and homogeneous nucleators (diamide segments in the chain).^{6,7}

The nucleating effect of diamide segments incorporated in PET was recently shown^{2,6,7}; the most effective diamide is based on ethylene diamine (T2T, see structure below),⁷ probably because it has a length similar to the ethylene glycol (EG) unit of PET. The incorporation of only 0.1 mol % T2T into PET decreases the undercooling ($T_m - T_c$) from 74 to 54°C.⁷



T2T segment

The diamide units self-assemble in the melt phase by hydrogen bonding and therefore the entropy of crystallization is lower in PET containing diamide units.⁷

All the above-mentioned nucleators improve the rate of crystallization, but compared to PBT, the actual rates are still not very high. Given that the mechanisms of nucleation are different, one might ask if there is any synergy in the rate of crystallization between the methods and, in particular, whether any synergy can be obtained by the introduction of diamide units, as well as short and long codiols.

PET Containing Short Codiols

Short codiols usually disturb the order of PET; but, surprisingly, when they are present in small quantities, they are able to act as nucleators.³ Codiols ($C > C_4$) fold easily and have a lower surface tension than ethanediol.^{3,8} The codiols are not incorporated in the crystalline phase because they do not fit into the crystalline lattice of PET and are present in the amorphous phase. The codiols are possibly also partly present in the chain fold and thereby lower the free energy of the fold surface, resulting in an increase in the nucleation rate. According to Hofman et al.,⁹ the free energy of the fold surface is given by the following equation:

$$\sigma_E = \frac{\varphi}{2A_0} \quad (1)$$

in which φ is the energy required for the polymer chain to fold and A_0 is the effective chain cross

section in the crystal. Branched diols such as 2,5-hexanediol and 3-methyl-2,4-pentanediol are particularly effective, and the optimum concentration is in the range of 5 mol %.³ Branched diols have methyl side groups; it is probable that these pending groups decrease the surface free energy to a greater extent than linear diols. At higher concentrations, the disturbance of the chain order dominates the crystallization and the crystallization rates are then reduced.

By decreasing the surface free energy of the fold, the critical size of a nucleus is decreased such that nucleation then takes place more easily. The surface free energy is one of the parameters in the isothermal nucleation rate (\dot{N}) shown in expression (2)^{10,11}:

$$\dot{N} = \dot{N}_0 \exp\left(-\frac{C_1}{R(C_2 + T - T_g)}\right) \times \exp\left(-\frac{32\sigma^2\sigma_E T_m^4}{k(\Delta H_f)^2 T^3 (\Delta T)^2}\right) \quad (2)$$

where N_0 , C_1 , C_2 , k , and R are constants; ΔH_f is the heat of fusion; σ is the surface free energy in the radial direction; and σ_E is the surface free energy in the growth direction. The other parameters are the viscosity related $T - T_g$ and the undercooling temperature of crystallization ΔT ($T_m - T_c$). The ($T_m - T_c$) value in a dynamic experiment is often taken as a measure for the ease of crystallization.

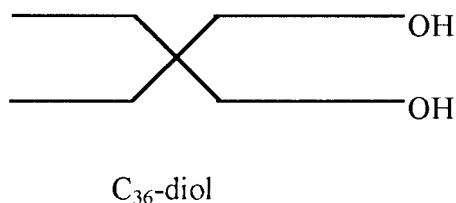
During the synthesis of PET, the dimer of EG, diethylene glycol (DEG), is always formed, such that PET usually contains between 2 and 4 mol % DEG. The glass-transition temperature (T_g), as well as the melting temperature (T_m), of PET are known to be decreased with increasing DEG content; however, the effect of DEG on the rate of crystallization is minimal.^{12,13}

PET Containing Long Codiols

PET can be modified using a small amount of polyether segments to form segmented copolymers having a lower T_g (PET is internally plasticized).⁵ Lowering the T_g allows the use of lower mold temperatures; this is an advantage because the usual mold temperatures required for PET are very high (120–40°C) and are therefore impractical.¹⁴ PET can be modified with the polyethers poly(ethylene glycol) (PEG) and poly(buty-

lene glycol) (PBG)^{4,5,13}; unfortunately these polyethers are thermally unstable.

The modification of PET with an olefinic diol (C_{36} -diol) is new. The C_{36} -diol (below) is a branched alkane with a functionality of approximately 2. The C_{36} -diol is more thermally stable than PEG and PBG segments and is therefore possibly better suited for use in high melting PET, if it forms one amorphous phase with PET. When the C_{36} -diol is copolymerized with PBT, the segmented copolymer has one T_g .¹⁵



The aim of this work was to investigate the effect of codiol incorporation on the crystallization and thermal properties of PET. The linear, branched, and aromatic codiols were compared: 1,5-pentanediol, 1,8-octanediol, 2,5-hexanediol, and 1,3-dihydroxymethyl benzene. The possible synergy between the codiols and the diamide segment T2T was also studied to further increase the rate of crystallization. In addition, the effect of the C_{36} -diol on the thermal properties and crystallization behavior of PET was examined.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT), 1,2-ethanediol, 2,5-hexanediol, 1,5-pentanediol, 1,8-octanediol, 1,3-dihydroxymethyl benzene, and $Ti(i-OC_3H_7)_4$ were purchased from Merck and used as received. The titanium catalyst $Ti(i-OC_3H_7)_4$ was diluted in anhydrous *m*-xylene (0.1M). The C_{36} -diol was obtained from Uniqema, Gouda (The Netherlands), and the T2T-dimethyl was synthesized and purified as previously described.¹⁶

Melt Polymerization

The preparation of PET with 0.1 mol % T2T-dimethyl and 5 mol % 1,5-pentanediol is discussed as an example. The reaction was carried out in a 250-mL stainless steel vessel with a nitrogen inlet and mechanical stirrer. The vessel containing the DMT (29.07 g, 150 mmol), T2T-

dimethyl (0.058 g, 0.15 mmol), 1,2-ethanediol (20.00 g, 323 mmol), and 1,5-pentanediol (0.78 g, 7.5 mmol) was heated in an oil bath to 180°C and the catalyst solution then added (3 mL). After a 50-min reaction time, the temperature was raised to 280°C (15°C/10 min); after a further 10 min at 280°C the pressure was reduced over a period of 5 min to 20 mbar and then further reduced over 15 min to less than 1 mbar. Finally, the vessel was cooled to room temperature while maintaining the low pressure.

Solid-State Postcondensation

The polymer was ground in a Fritsch Pulverisette (particle size < 1 mm) and subsequently dried in a vacuum oven at 70°C overnight. Over a period of 24 h the polymer was postcondensed in the solid state at a reduced pressure (<0.1 mbar) in a glass tube that was placed in an oven at 225°C.

Viscometry

The inherent viscosity of the polymers at a concentration of 0.1 g/dL in *para*-chlorophenol at 45°C was determined using a capillary Ubbelohde 1B.

Differential Scanning Calorimetry (DSC)

The DSC spectra were recorded on a Perkin-Elmer DSC7 apparatus equipped with a PE7700 computer and TAS-7 software. Dried samples of 2–5 mg were measured at a cooling and heating rate of 20°C/min. The samples were heated to 320°C; this temperature was maintained for 2 min followed by cooling to 20°C with the maximum of the cooling scan being taken as the T_c . After 2 min at 20°C, the sample was heated for a second time to 290°C; the maximum of the second heating scan was taken as the T_m . The peak area was used to calculate the enthalpy.

Dynamic Mechanical Analysis (DMA)

Samples for the DMA tests (70 × 9 × 2 mm) were prepared on an Arburg H manual injection molding machine. The barrel temperature of the injection molding machine was set at 50°C above the T_m of the polymer, and the mold temperature was 150°C. The mold was opened after 2 min. Using a Myrenne ATM3 torsion pendulum at a frequency of approximately 1 Hz, the values for the storage modulus G' and the loss modulus G'' as a function of the temperature were then measured.

Table I DSC (20°C/min) Results of Thermal Properties of PET and PETA_{0.1}, and Copolymers with Different Codiols

| Codiol | Polymer | Concn (mol %) | DEG (mol %) | η_{inh} (dL/g) | T_m (°C) | ΔH_m (J/g) | T_c (°C) | ΔH_c (J/g) | ΔT (°C) |
|-----------------|---------------------|---------------|-------------|---------------------|------------|--------------------|------------|--------------------|-----------------|
| None | PET | — | 3.0 | 0.99 | 254 | 52 | 180 | -38 | 74 |
| None | PETA _{0.1} | — | 1.0 | 1.03 | 264 | 45 | 210 | -51 | 54 |
| 1,5-Pentanediol | PET | 0.6 | | 0.71 | 260 | 42 | 201 | -47 | 59 |
| 1,5-Pentanediol | PETA _{0.1} | 1.1 | 1.8 | 0.67 | 260 | 49 | 204 | -51 | 56 |
| 1,5-Pentanediol | PET | 6.0 | | 1.07 | 248 | 43 | 186 | -44 | 62 |
| 1,5-Pentanediol | PETA _{0.1} | 6.0 | 1.7 | 1.06 | 253 | 44 | 194 | -47 | 59 |
| 1,5-Pentanediol | PETA _{0.1} | 8.5 | 0.6 | 0.71 | 245 | 40 | 184 | -45 | 61 |
| 1,3-DHMB | PET | 0.5 | 1.6 | 1.09 | 260 | 48 | 194 | -50 | 66 |
| 1,3-DHMB | PETA _{0.1} | 0.5 | | | 262 | 52 | 204 | -50 | 58 |
| 1,3-DHMB | PETA _{0.1} | 2.3 | 1.6 | 0.80 | 259 | 50 | 200 | -48 | 59 |
| 1,3-DHMB | PETA _{0.1} | 5.0 | 2.8 | 0.64 | 250 | 43 | 192 | -44 | 58 |
| 1,3-DHMB | PET | 5.6 | 0.9 | 0.85 | 252 | 39 | 185 | -45 | 67 |
| 1,3-DHMB | PETA _{0.1} | 8.4 | 1.4 | 0.61 | 243 | 21 | 184 | -22 | 59 |
| 2,5-Hexanediol | PET | 0.6 | 1.0 | 0.73 | 262 | 51 | 205 | -65 | 57 |
| 2,5-Hexanediol | PETA _{0.1} | 0.8 | 1.2 | 0.62 | 263 | 60 | 209 | -53 | 54 |
| 2,5-Hexanediol | PET | 1.0 | | 0.65 | 262 | 51 | 206 | -52 | 56 |
| 2,5-Hexanediol | PETA _{0.1} | 1.7 | 0.9 | 0.53 | 261 | 51 | 207 | -52 | 54 |
| 2,5-Hexanediol | PET | 1.8 | 1.2 | 0.56 | 261 | 47 | 199 | -50 | 62 |
| 1,8-Octanediol | PETA _{0.1} | 5.0 | 1.6 | 1.79 | 250 | 55 | 194 | -51 | 56 |

1,3-DMMB, 1,3-dihydroxymethylbenzene.

Dried samples were first cooled to -100°C and then subsequently heated at a rate of 1°C/min. The maximum of the loss modulus was taken as the T_g . The flow temperature (T_f) was defined as the temperature where the storage modulus reached 15 MPa.

NMR Analysis

Proton NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1 MHz. Deuterated trifluoroacetic acid was used as a solvent in the absence of an internal standard.

RESULTS AND DISCUSSION

In this article we report about the synthesis and properties of copolymers of PET or PETA_{0.1} (PET with 0.1 mol % T2T) and a codiol or C₃₆-diol. Previous research showed that PETA_{0.1} crystallizes faster than PET.⁷ The effect of the type of codiol used and its concentration in PET or PETA_{0.1} on the thermal properties of PET was studied. The DEG content of the copolymers was approximately 0.5–3 mol %; in this concentration range the effect of the DEG content on the crystallization of PET is small.¹³

Incorporation of Codiols

A number of different codiols were incorporated into PET and PETA_{0.1} in a concentration range of 0–10 mol %. The copolymers were synthesized using a titanium catalyst, and the results of the postcondensed polymers are presented in Table I. The codiol and the DEG content were determined by ¹H-NMR, and the effects of the composition on the crystallization and melting temperatures were studied by DSC.

The inherent viscosities of the polymers incorporating 1,5-pentanediol were found to be reasonably high and comparable to those of PET. Figure 1 plots the T_m and T_c of PET versus the 1,5-pentanediol content as measured by DSC at a heating and cooling rate of 20°C/min. At low concentrations (<1 mol %), the incorporation of 1,5-pentanediol into PET leads to an increase in the T_m and T_c , and the increase in T_c is greater than in T_m . At higher concentrations the T_m and T_c decrease again. The effect of 1,5-pentanediol on the undercooling ($T_m - T_c$) of the polymers is shown in Figure 2. The undercooling of PET copolymers decreases upon the incorporation of a small amount of 1,5-pentanediol, but when increasing the concentration the undercooling again increases. The incorporation of 1,5-pen-

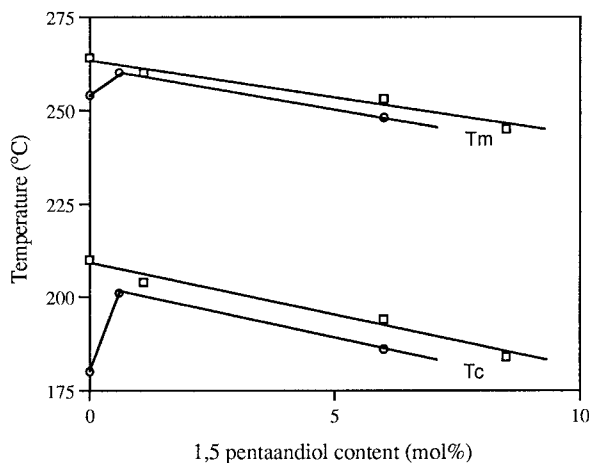


Figure 1 The melting (T_m) and crystallization (T_c) temperatures versus the 1,5-pentadiol content in (○) PET and (□) PETA_{0.1}.

tanediol increases the nucleation rate of PET at low codiol concentrations but disturbs the chain order at higher concentrations; thus, there is an optimum codiol concentration at around 1 mol %.

The PETA_{0.1} crystallized more rapidly than PET and the incorporation of 1,5-pentadiol had no additional positive effect on the T_m or T_c or the undercooling. The incorporation of 1,5-pentadiol in PETA_{0.1} showed that there was no synergy between the T2T and the codiol in the nucleation. The melt and crystallization enthalpies of PET and PETA_{0.1} were found to decrease on increasing the 1,5-pentadiol content (>5 mol %), which was due to the crystallinity being lowered by the disturbance in the chain order.

A number of other diols were also studied; these included the partial aromatic 1,3-dihydroxymethyl benzene, the branched 2,5-hexanediol, and the linear 1,8-octanediol. The branched 2,5-hexanediol should, according to Bier et al.,³ be an effective nucleator at a concentration of 5 mol %. The partial aromatic 1,3-dihydroxymethyl benzene and 1,8-octanediol are able to fold easily, and this should also be an advantage for the crystallization.⁸ The PET containing 2,5-hexanediol had a higher T_c and was therefore slightly better than the linear 1,5-pentadiol at improving the crystallization of PET; the optimum concentration for 2,5-hexanediol was shown to be 1 mol % (Table I). This concentration was much lower than the 5% previously reported.³ Incorporation of the partial aromatic 1,3-dihydroxymethyl benzene into PET did not increase the T_c to the same extent as the 1,5-pentadiol or 2,5-hexanediol. It was also found that the copolymer of

PETA_{0.1} containing 1,8-octanediol had a T_c value similar to the other aliphatic diols in PETA_{0.1}.

Of the codiols studied here, 2,5-hexanediol seemed to be the most effective in the nucleation of PET, but only at very low concentrations (1 mol %). This codiol was also tested in PBT, but there was only a small effect on the T_m , T_c , and T_g values. Because PBT itself is a rapidly crystallizing polymer, no additional benefit of adding a nucleating codiol could be observed.

Incorporation of C₃₆ Segments

The chain flexibility of the amorphous phase of PET can be increased by the incorporation of long segments. We studied the effect of C₃₆-diol incorporation on the crystallization and thermal properties of the PET-C₃₆ copolymers. When the C₃₆-diol was copolymerized with PBT, one T_g was observed; and at a high C₃₆ concentration the T_g approached -55°C .¹⁵ We synthesized copolymers of PET and PETA_{0.1} using increasing amounts of C₃₆-diol, the results of which are presented in Table II. In Figure 3 the storage moduli of the PETA_{0.1} copolymers are plotted against the temperature for various C₃₆-diol concentrations. These copolymers have only one T_g , indicating that the amorphous phases of PET and the C₃₆-diol are fully miscible. In Figure 4 the T_m , T_c , and T_g values of the PET copolymers are plotted versus the C₃₆-dimerized diol content. The incorporation of the C₃₆-diol into PET has a great effect on the T_g value, and the T_g decreases linearly with increasing C₃₆ content. The T_m and T_f also decreased slightly with the C₃₆-diol content. In

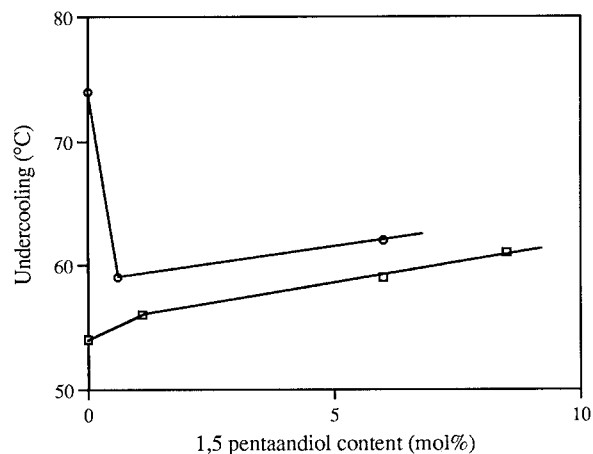


Figure 2 The undercooling ($T_m - T_c$) versus the 1,5-pentadiol content in (○) PET and (□) PETA_{0.1}.

Table II DSC (20°C/min) and DMA Results of PET and PETA_{0.1} with C₃₆-Diol

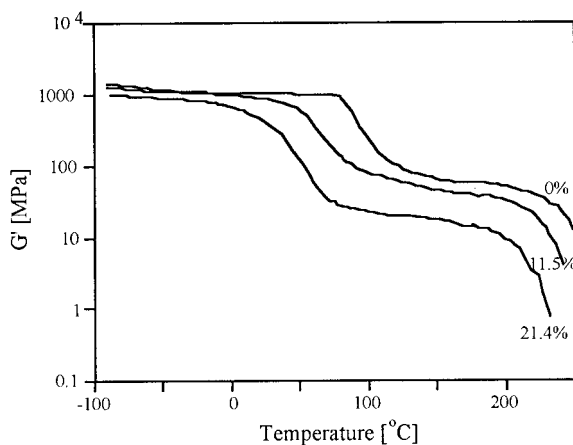
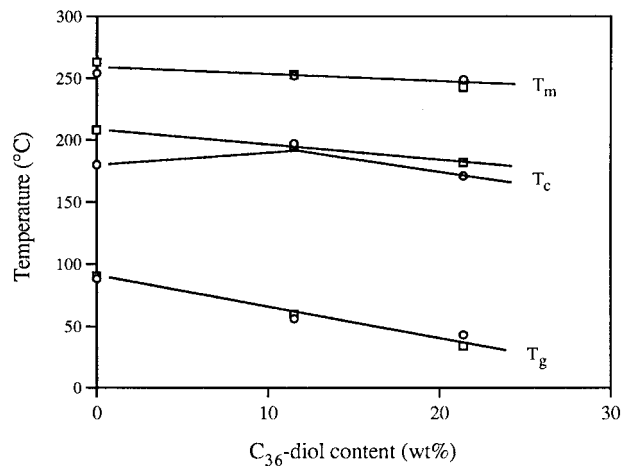
| C ₃₆ -Diol | | Polymer | η_{inh} (dL/g) | T_m (°C) | ΔH_m (J/g) | T_c (°C) | ΔH_c (J/g) | ΔT (°C) | T_g (°C) | T_f (°C) |
|-----------------------|-------|---------------------|------------------------|---------------|-----------------------|---------------|-----------------------|--------------------|---------------|---------------|
| wt % | mol % | | | | | | | | | |
| 0 | 0 | PET | 0.99 | 254 | 52 | 180 | -38 | 74 | 88 | 244 |
| 0 | 0 | PETA _{0.1} | | 263 | 50 | 208 | -51 | 55 | 90 | 247 |
| 11.5 | 5 | PET | 0.74 | 252 | 54 | 197 | -51 | 55 | 56 | 238 |
| 11.5 | 5 | PETA _{0.1} | 0.78 | 253 | 46 | 195 | -46 | 58 | 60 | 239 |
| 21.4 | 10 | PET | 0.99 | 249 | 38 | 171 | -47 | 79 | 43 | 236 |
| 21.4 | 10 | PETA _{0.1} | 1.32 | 243 | 38 | 182 | -35 | 61 | 34 | 232 |

the modified PET materials the T_c was found to first increase, but at high concentrations of C₃₆-diol it decreased again. This effect on the T_c was similar to that when using short codiols as described above. This means that with 11.5 wt % (5 mol %) C₃₆-diol, the crystallization rate was enhanced, because of the higher T_c and the lower T_g . The C₃₆-diol copolymers based on PETA_{0.1} had T_g and T_m transitions similar to those based on PET, and the effect of T2T was overshadowed by the presence of the C₃₆-diol.

The temperature region between the T_m and T_g is the crystallization window and, according to eq. (2), this can also be represented as a T_g/T_m ratio.¹¹ Van Krevelen¹⁷ showed that the $T_{c,max}/T_m$ ratio increases almost linearly with the T_g/T_m ratio. The $T_{c,max}$ is the temperature at which the crystal growth rate is at its maximum, and for PET the $T_{c,max}$ value is 175°C.^{10,11} With a lower T_g/T_m ratio, a lower value for the $T_{c,max}/T_m$ ratio is obtained and the crystallization window is thereby widened; as a result, a more rapidly crys-

tallizing material is expected. The T_g/T_m ratio versus the amount of C₃₆-dimerized diol is shown in Figure 5. It can be seen that the T_g/T_m ratio decreases appreciably with an increasing C₃₆-diol content; this is the case for both for PET and PETA_{0.1} C₃₆-diol copolymers.

Another difficulty in the crystallization of PET during injection molding is the high temperature at which crystallization takes place and therefore the impractical high molding temperature.¹⁴ The molding temperature depends on both the $T_{c,max}$ and the T_g and for PET it has to be above 120°C, so that oil-heated molds have to be used. Given that when the C₃₆-diol is incorporated into PET the T_c can be increased, the T_g decreased, and the T_g/T_m lowered, a more rapidly crystallizing material can be obtained that can possibly be processed with a lower mold temperature. The C₃₆-diol is effective in increasing the crystallization window of PET at concentrations up to 11.5 wt % (5 mol %).

**Figure 3** The storage modulus (G') versus the temperature of PETA_{0.1} C₃₆-diol polymers (wt % C₃₆-diol).**Figure 4** The T_m , T_c , and T_g of (○) PET and (□) PETA_{0.1} copolymers versus the C₃₆-diol content.

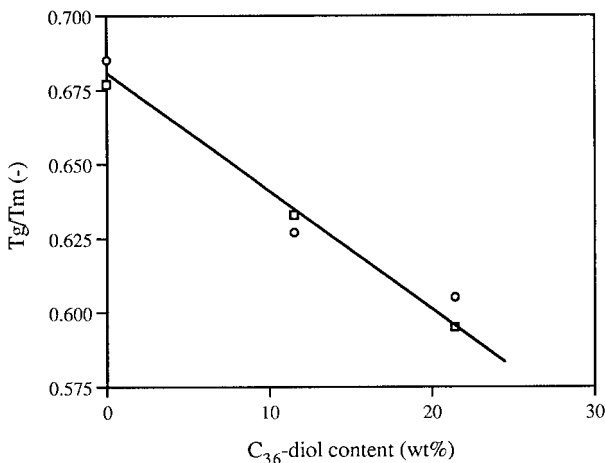


Figure 5 The T_g/T_m ratio of (○) PET and (□) PETA_{0.1} copolymers versus the C₃₆-diol content.

CONCLUSIONS

Codiols were able to improve the nucleation of PET by lowering the interfacial free energy; thus, crystallization nuclei were formed more rapidly. However, the presence of codiols also disturbed the chain order and had a negative effect on the crystallization rate. Therefore, there was an optimum codiol concentration, which was found to be at approximately 1 mol %; this was lower than the 5% previously reported.³ The branched 2,5-hexanediol was the most effective PET nucleating codiol; however, the incorporation of codiols into PETA_{0.1} had no additional positive effect, in that there was no synergy between the diamide effect and the codiol effect. It was also found that T2T was a more efficient PET nucleator than codiols. The T2T units and the diol groups increased the nucleation rate but probably not the growth rate and are therefore not synergistic.

Only one T_g was observed when long diol segments (C₃₆-diol) were incorporated into PET, and the T_g was found to decrease with increasing C₃₆-diol concentration, C₃₆-diol being an internal plastifier for PET. The T_m was found to be only slightly lowered and the T_c was increased at low diol concentrations (<10 wt %). By increasing the T_c and lowering the T_g , the window between the T_g and T_c could be widened, thereby increasing the ability to crystallize and thus allowing the use of lower mold temperatures. Because incorporat-

ing C₃₆-diol caused the crystallization window to increase, not only the nucleation rate but probably also the crystallization rate was increased.¹¹ Given that for stiffness reasons the T_g of the modified PET should not drop below 50°C, the concentration range of interest for the use of the thermally stable C₃₆-diol was up to 11.5 wt %.

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