Branched Poly(ethyleneterephthalate)

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Several batches of branched poly(ethyleneterephthalate) (PET) of varying degrees of branching were prepared, using common PET monomers and special branching monomers synthesized by us. For the purpose of originality the trifunctional branchpoints currently employed by various industrial manufacturers were avoided and only tetra-, hexa- and octa-functional branching monomers were created and incorporated into the PET chains. The combination of intrinsic viscosity (I.V.) and light scattering measurements indicates that, as expected, higher functionality branchpoint monomers are more effective branching agents than their lower functionality analogues, and the molecular weight within each series of branched PET increases with increasing concentration of branching residues. Increasing amounts of microgels appear in the preparations as the concentration increases of effective branchpoint residues in the branched PET.

Keywords: Poly(ethyleneterephthalate); PET; Branching; Polymer synthesis; Viscosity-average molecular weight; Weight-average molecular weight; Melt elasticity; Melt viscosity; Branched PET

INTRODUCTION

Due to its relatively low molecular weight (MW) and short chain length, poly(ethyleneterephthalate) (PET) is generally considered to be a semi-crystalline polymer of rather low melt viscosity and elasticity. While the low melt viscosity makes injection molding and melt spinning more facile, the associated low melt elasticity increases the drooling of the molten polymer and renders operations such as blow molding of large and/or complex-shaped containers almost impossible. These processes require polymers of relatively high melt elasticity in

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order to succeed. The desired combination of properties, *i.e.*, low melt viscosity together with high melt elasticity, actually exists in polymers employed in the creation of large and complex containers by blow molding operations such as polyethylene (PE) of MW far higher than is common in PET.

In the case of PET, one way to obtain a polymer with high melt elasticity is to create PET with very long linear chains. Because of the very large chain end-to-end distance associated with very long chains, the result is a polymer with very high melt viscosity; an undesired property. Another way to obtain PET with high melt elasticity is to create macromolecules each containing a small number of branch-points, such that the resulting macromolecule will contain a small number of relatively long branches. Because such macromolecules will have smaller end-to-end distance than their linear analogues of identical MW, they are expected to have melt viscosity lower than the melt viscosity of the linear chains. At the same time, the melt elasticity of the branched PET is expected to remain high due to interchain entanglements with other macromolecules containing long branches. The lower melt viscosity carries over to lower solution viscosity. This results in calculated viscosity average molecular weight, M_v, lower than the correct value. On the other hand, the weight average molecular weight, M_w, obtained from light scattering measurements, is independent of branching. Therefore, the ratio M_w/M_v, which is about 1.2 for linear polymers, is expected to increase above it as a function of branching.

Below, it will be shown how to create branched PET macromolecules by the use of novel 4-arm, 6-arm, and 8-arm branchpoints. Because of their novelty, the preparation of the branching monomers by several synthetic routes will be described in detail. A typical polymerization of branched PET will then be described. The results will then be presented and their significance briefly discussed.

EXPERIMENTAL

Synthesis

All reagents and solvents were purchased from chemical supply houses at the highest available purity, kept under anhydrous conditions, and

used with no further purification. Following are examples of branchpoint monomer syntheses.
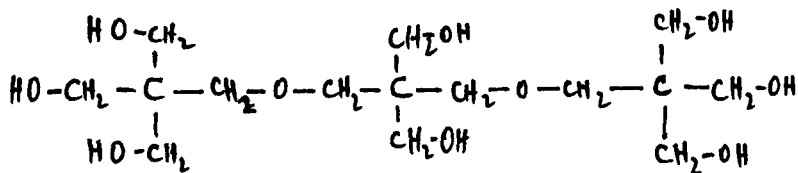
(1) Amide 4-arm branchpoints by the Yamazaki [1, 2] method: 0.1 moles of dimethyl-5-aminoisophathalate and 0.05 moles terephthalic acid (TPA) were dissolved with constant stirring and heating at about 105–110°C in about 200 mL N,N-dimethylacetamide (DMAc) containing slightly over 0.1 moles pyridine. When the dissolution was complete, slightly over 0.1 moles of triphenylphosphite (TPP) were added. The reaction was continued at the above temperature for 3 more hours. The heating was then stopped and the reaction mixture carefully poured with swirling into 2 liters of methanol. After about 30 minutes of stirring, the solid precipitate was filtered off through a fritted glass funnel, and the damp solids suspended twice, each in over 1 liter methanol, and filtered, prior to finally drying by means of air stream and then overnight in a vacuum oven under dynamic vacuum of less than 10 mm Hg at about 100°C. The yield was over 90% of theory.

(2) Amide 4-arm branchpoint by means of Schotten-Baumann reaction: 0.1 moles of dimethyl-5-aminoisophthalate were dissolved with constant stirring in about 200 mL of a 1:1 vol/vol mixture of 1,2-dichloroethane (DCE) and pyridine at room temperature. To this stirred mixture, a solution of 0.05 moles terephthaloyl chloride in about 60 mL DCE was added dropwise from a dropping funnel. The temperature of the swirling reaction mixture was maintained below room temperature by immersing the reaction flask in an ice–water bath. With the progress of the reaction a precipitate formed. With stirring, the reaction was allowed to continue for additional 3–4 hours. Then, the mixture was poured into a large excess of acetone and filtered through a fritted glass funnel. The residual DCE was allowed to evaporate off, and the solids were then washed first with water, followed by water/methanol mixture, and finally with methanol. The solids were then dried overnight in a vacuum oven at about 100°C. The yield was over 85% of theory.

(3) Amide 6-arm branchpoint by the Yamazaki [1, 2] procedure: in a fashion similar to example (1) above, in a 500 mL round bottom flask, there were 0.15 moles of dimethyl-5-aminoisophathalate

and 0.05 moles of 1,3,5-benzenetricarboxylic acid dissolved with constant stirring and heating at 110°C in about 300 mL DMAc containing 0.15 moles pyridine. After the dissolution was complete, 0.15 moles of TPP were added to the stirred reaction mixture. The reaction was allowed to continue at temperature for 3 additional hours prior to termination. Once the reaction mixture cooled to below 100°C, it was poured with rapid stirring into 2 liters methanol. When the precipitation was complete, the suspension was filtered through flitted glass funnel. The solids were then washed two or three times in large excess of methanol and filtered, until the odor of pyridine or phenol was completely absent. The solids were then air dried prior to an overnight drying in vacuum oven as described above.

(4) Amide 6-arm branchpoint by Schotten-Baumann reaction: in a fashion similar to example (2) above, there were dissolved 0.15 moles of dimethyl-5-aminoisophthalate in about 300 mL of a mixture of DCE and pyridine. The amount of pyridine was dictated by its ability to completely dissolve the monomer. Once the monomer was fully dissolved, additional 0.15 moles of pyridine were added in order to serve as HCl receptor in the Schotten-Baumann reaction. The solution was constantly stirred and its temperature maintained at below room temperature by placing the round bottom reaction flask in a bath full of ice and water. In a pressure equalizing funnel, a solution of 0.05 moles of 1,3,5-benzenetricarboxylic acid chloride in 100 mL DCE was prepared. This solution was then added dropwise to the stirring solution of the amine. After the addition was completed, the resulting slurry was stirred at room temperature for 3 additional hours before the reaction was terminated. The mixture was then poured into a large excess of methanol and filtered. The solids were repeatedly washed in methanol and acetone prior to drying as described above.

(5) Ester 4-arm branchpoint by Schotten-Baumann reaction: in a round bottom flask equipped with magnetic stirrer and immersed in a thermostated oil bath, there were dissolved with stirring and heating at about 80°C 0.1 moles of dimethyl-5-hydroxyisophthalate in a mixture of DCE and pyridine. The pyridine was used in large excess in order to facilitate the dissolution of the monomer,

and even so the mixture had to be kept hot in order to keep all the monomer in solution. In a separate vessel, there were dissolved 0.05 moles of terephthaloyl chloride in about 100 mL DCE at ambient temperature. This solution was then added from a pressure equalizing funnel to the stirring hot solution in the round bottom flask in a rapid drop-wise manner. After the addition was complete, the resulting hot hazy solution was allowed to stir for an extra three and a half hours before the reaction was terminated. Upon cooling, the 4-arm ester precipitated out and was filtered off. It was then washed with acetone, then with water and finally with methanol. The absence of pyridine odor served to indicate the purity of the product. Drying was accomplished as described above.

(6) Ester 6-arm branchpoint by Schotten-Baumann reaction: this was achieved as indicated in example (5) above, except for the substitution of terephthaloyl chloride by 1,3,5-benzenetricarboxylic acid chloride, and a change in the molar ratio of the monomers to 3:1 dimethyl-5-hydroxyisophthalate/1,3,5-benzenetricarboxylic acid chloride. All other details of the procedure remained essentially the same.

(7) Ester 6-arm branchpoint by interfacial reaction: in about 100 mL of water there were placed 0.126 moles of dimethyl-5-hydroxyisophthalate and 0.132 moles KOH. After a few minutes of stirring, the dimethyl-5-hydroxyisophthalate reacted with the KOH and completely dissolved in the water. The solution was placed in the container of an Oster blender. A solution of 0.04 moles of 1,3,5-benzenetricarboxylic acid chloride in 100 mL dichloroethane was separately prepared. The organic solution was then rapidly added to the intensely agitated aqueous solution in the blender, and the agitation continued for about 10 additional minutes. Copious amounts of solids appeared in the system. After the DCE evaporated, the solids were filtered off and repeatedly washed with water to remove the residual base. The resulting solid product was then washed with methanol and finally dried as described above. The yield was a little over 70% of theory. 4-Arm ester branchpoint may be prepared in similar fashion.

(8) Ether 8-arm branchpoint by transesterification: in this case the 8-branch molecule tripentaerythritol (TPE)

$$
\begin{array}{ccc}
HO-CH_2 & CH_2OH & CH_2-OH \\
| & | & | \\
HO-CH_2-C-CH_2-O-CH_2-C-CH_2-O-CH_2-C-CH_2-OH \\
| & | & | \\
HO-CH_2 & CH_2-OH & CH_2-OH
\end{array}
$$

Tripentaerythritol

was used as the starting material. In a polymerization kettle there were placed 0.1 moles of TPE, 0.8 moles of dimethylterephthalate (DMT) and about 2 moles of ethylene glycol (EG) together with a catalytic amount of zinc acetate. The kettle was closed, a stream of nitrogen passed through, and the temperature elevated to about 180°C. After the DMT melted, the reaction mixture was constantly stirred by means of a mechanical stirrer and the temperature maintained in the 180–210°C interval throughout the reaction. After a few minutes, methanol started distilling off in the nitrogen stream, which was collected to gauge the progress of the reaction. The reaction was allowed to continue for an hour after about 0.8 moles methanol were collected. The reaction mixture was then cooled to below 100°C before it was poured into a large amount of water. The solids, which consisted mostly of the desired 8-arm ether, were filtered off the water. They were then washed with cold methanol, prior to drying under vacuum. Integration of the areas under the respective NMR resonance peaks indicated that the solid product contained the expected amounts of one tripentaerythritol, about eight terephthalate residues, and about 8 ethylene glycol residues. The large majority of the latter were linked to the terephthalate at one end and were terminated with a free —OH on the other end. The 8-arm tripentaerythritol-terephthalate-glycolate product was used as obtained without further purification.

Example of typical polymerization (sample # 4B): in a 500 mL polymerization kettle equipped with a 4-neck top, a high torque mechanical stirrer, a nitrogen inlet, a nitrogen outlet that doubles as a connection to a vacuum pump through a distillation head with a long condensation arm, there were placed 0.87 grams (0.223 mole%) of

the amide 6-arm branchpoint monomer (molecular weight 783.7 g), 98 grams DMT (0.5 moles), about 78 grams ethylene glycol (1.25 moles), 0.55 grams of the transesterification catalyst zinc acetate and 0.40 grams of the polycondensation catalyst germanium dioxide. The kettle was placed in a controlled temperature oil bath, connected to the nitrogen/vacuum ports, and purged with nitrogen. Then the temperature was brought up over 1 hr to around 190°C where the distillation of methanol commenced. After essentially all the theoretically expected methanol was distilled off, the molten reaction mixture was stirred at the same temperature under a slow stream of nitrogen for additional 30 minutes. The temperature was then increased over 1 hr to 270°C. Ethylene glycol was distilled off in a slow stream of nitrogen at this temperature for one additional hour. The nitrogen was then disconnected, vacuum was gradually applied and the temperature further increased to 275°C during additional 30 minutes. Then, a vacuum of ca. 1 mm Hg was applied by the vacuum pump and the reaction continued for additional 10–15 minutes. In this fashion, the boiling EG and molten PET do not splatter all over the top parts of the reaction kettle and all the catalysts and reactants remain in the molten polymerizing mass. Upon termination, the vacuum is broken by the introduction of nitrogen, the polymerization kettle rapidly disassembled, and the molten polymer rapidly removed with the help of many spatulas directly into a bath of "dry ice". When the polymer's temperature approaches that of solid carbon dioxide, all the solids are ground together in a Wiley mill. The "dry ice" is then allowed to sublime and the polymer collected and dried first in an air stream and finally overnight in a vacuum oven at a temperature of about 110°C. In order to prepare linear PET, the above polymerization procedure is identically maintained with the omission of the branchpoint molecules.

Characterization

Intrinsic viscosity (I.V.) measurements were conducted on solutions of the polymer samples in 60:40 phenol/tetrachloroethane mixture at 25°C using internal dilution Cannon-Ubbelohde glass viscometers with efflux time not shorter than 100 seconds. The viscosity average molecular weight, M_v, of the samples was calculated from their

I.V. values by means of the following Mark-Houwink-Sakurada equation:

$$\text{I.V. (in dL/g)} = 2.37 \times 10^{-4} M_v^{0.73}.$$

Low angle laser light scattering (LALLS) measurements were performed at 25°C on solutions of the polymers in the same solvent mixture used for I.V. determinations, using a Chromatix KMX-6 instrument. The solvent mixture and solutions were kept under anhydrous conditions. They were all filtered through anodisc filters with 200 nm pore size to remove any particulate impurities in the solvent and polymeric microgels having diameters larger than the pore size. From the scattered light intensities at several angles the weight average molecular weight, M_w, of the samples were calculated in the customary manner.

RESULTS AND DISCUSSION

The branched and linear PET samples synthesized in the course of this work were all prepared by a melt polymerization procedure well known in the art [3]. In order to avoid the precipitation of small particles of elemental antimony that lead to the graying of the polymers and may interfere with the light scattering measurements, non-antimony catalysts were used. For the transesterification, zinc acetate served as the catalyst, and germanium dioxide served to catalyze the subsequent polycondensation step. All diacid and poly-acid monomers were introduced in the form of their methyl esters. For the purpose of comparing the various runs and evaluating the effects of the branchpoint-generating monomers, the profiles of nitrogen flow, rpm of the mechanical stirrer, vacuum application, and thermal ramping were kept identical for all polymerization. This by no means implies that minor deviations did not occur of individual polymerization conditions from the desirable more stringent conditions. When such deviations occurred, they usually involved momentary over-shoots of the kettle temperature above the set-temperature. This was generally corrected within less than 5 minutes.

There were altogether five different branchpoint generating mol-
ecules used in the creation of the branched PET. They are:

4-arm amide

4-arm ester

6-arm amide

6-arm ester

8-arm ether
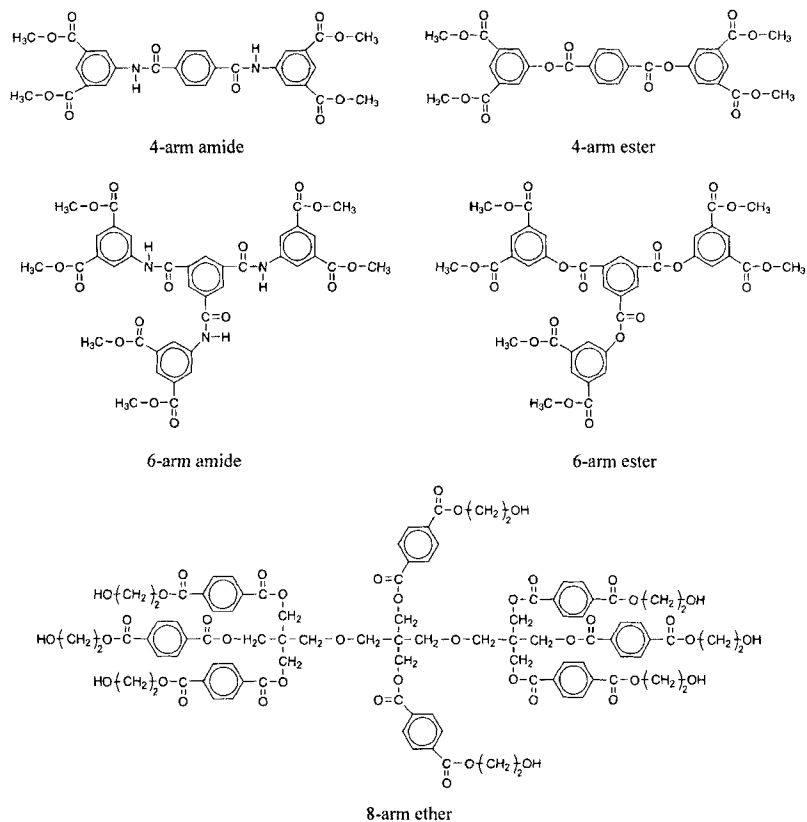
The polymer samples prepared using these branchpoint-generating
molecules are listed in Table I together with the nature and con-
centrations of the branchpoint residues, their I.V. values in units
of dL/g, their M_v and M_w values, and the highly instructive M_w/M_v
ratios. From the characterization results presented in Table I, the
following facts may be established:

(a) The reproducibility of supposedly identical polymerization runs in
    our equipment and set-up is lower than that usually achieved in
    larger plants manufacturing PET on industrial scale [4, 5]. This is
    obvious from a comparison of the two linear polymers 1A and
    1B. However, the reproducibility is sufficient in order to draw

TABLE I   Viscosity and light scattering measurements of branched PET

Sample#	Branching agent	Mole%	I.V.*	M_v*	M_w**	M_w/M_v	Remarks
1A	None	0	0.766	64000	78000	1.22	Linear
1B	None	0	0.636	50000	63000	1.26	Linear
2A	4-arm amide	0.10	0.589	45000	55000	1.22	
2B	4-arm amide	0.33	0.560	42000	52000	1.24	
2C	4-arm amide	0.66	0.743	62000	100000	1.62	
3A	4-arm ester	0.10	0.705	57000	70000	1.23	
3B	4-arm ester	0.33	0.757	63000	79000	1.25	
3C	4-arm ester	0.66	0.805	69000	90000	1.30	
4A	6-arm amide	0.10	0.700	57000	84000	1.48	
4B	6-arm amide	0.223	1.250	130000	250000	1.95	
4C	6-arm amide	0.446	1.576	145000	330000	2.28	36.6% gels
5A	6-arm ester	0.10	0.940	85000	100000	1.20	
5B	6-arm ester	0.223	1.080	103000	126000	1.22	
5C	6-arm ester	0.446	1.361	185000	340000	1.84	ca. 50% gels
6A	8-arm ester	0.050	1.071	100000	123000	1.23	slight gels
6B	8-arm ester	0.075	0.933	82000	100000	1.22	6% gels
6C	8-arm ester	0.100	1.364	125000	187000	1.50	28% gels

*I.V. and M_v of soluble fraction only. Corrected for lowered concentrations caused by filtration of gels.
**M_w by low angle laser light scattering (LALLS). I.V. and light scattering measured in the same solvent.

conclusions with respect to the effects of the presence of branch-point monomers on the produced PET.

(b) The effects of the 4-arm amide and ester branchpoint monomers are rather small and only at the highest concentration used (0.66 mole%) an increase in M_w becomes noticeable.

(c) The 6-arm amide and ester branching agents are much more effective than their 4-arm counterparts in increasing the molecular weight and the branching of PET. The M_w of the PET is substantially larger than that of the linear analogues already at branchpoint monomers charges as low as 0.10 mole%. With increasing concentrations of the branchpoint monomers, not only M_w and M_v continue to grow substantially, but the ratios of M_w/M_v also grow, indicating increased branching. At the highest concentrations used of both amide and ester 6-arm branchpoint monomers, significant amounts of gels appeared in the system. Although undesirable for certain applications, such as melt spinning of fibers, the appearance of gels indicates that a large number of branched macromolecules are present in these polymers.

(d) The 8-arm ether molecules appear to be extremely effective branching agents for PET, and trace amounts of gels are observed in the branched PET with branchpoint monomer concentrations as low as 0.05 mole%.

(e) Within each series shown in Table I of branched PET, the degree of branching is directly related to the concentration of branchpoint monomer. This is especially noticeable in the case of the amide 6-arm branching agent where the M_w/M_v ratio shows dramatic growth with increasing branchpoint monomer concentration.

Considering together all the above results, one may conclude that the 6-arm amide and 8-arm ether branchpoint monomers are the most efficient branching agents from among the five different agents studied in this work.

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