Synthesis of Poly(ε-caprolactam) and Poly(ethyleneterephthalate) Star Polymers

S. M. Aharoni[a]

[a] AlliedSignal Inc. Research & Technology, Morristown, New Jersey, USA

PLEASE SCROLL DOWN FOR ARTICLE

Synthesis of Poly(ε-caprolactam) and Poly(ethyleneterephthalate) Star Polymers

SHAUL M. AHARONI

AlliedSignal Inc. Research & Technology, Morristown, New Jersey 07962, USA

Two kinds of condensation-polymerization star polymers were prepared. One kind is star nylon-6 and the other is star PET. In both star polymers the arms are flexible and the cores are rigid aromatic fractal polyamides (FPs). The FPs are porous and of size comparable to the size of the flexible arms of the stars. The FPs are decorated with reactive sites appropriate for the grafting or growing of star arms. In the case of star nylon-6, two preparation methods are described: grafting of pre-existing nylon chains onto FPs, and growing nylon-6 arms from the FPs by polymerization of caprolactam in the presence of FPs. In the case of star PET, grafting of pre-existing PET chains was employed in order to create the star polymers. Various characterization techniques indicated that in the grafted star polymers up to 10 arms could be attached to each FP core. The results indicate, however, that fine control of the star formaton was not achieved yet. The required conditions to reach this target are spelled out.

KEY WORDS Poly(ε-caprolactam), nylon-6, poly(ethyleneterephthalate), PET star-polymers, fractal polyamides, synthesis, graft-copolymer.

INTRODUCTION

Star-branched, or star-shaped, macromolecules are polymers containing three or more arms, all originating from the same point. In general, the arms of each star-polymer are flexible and their length is more or less identical. The point from which the arms of each star polymer originate is small relative to the length of the arms, and its influence on the static and dynamic properties of the polymer is generally disregarded. The vast majority of star-polymers reported in the literature fall into two categories of addition polymers: polyalkylenes [e.g., References 1–6] and polystyrenes [e.g., References 5 and 6]. The involved literature generally covers synthetic aspects, solution and rheological properties, and theoretical description of these star polymers. Unlike "dendrimers," characterized by multiple branchpoints on each of the arms originally emanating from the point of initiation, star-branched polymers have, in general, no branchpoints and the number of end-groups is identical to the number of arms originating from the "core" of each star-polymer. Recently, the synthesis and some properties of star-branched condensation polymer were reported in the literature,[7] namely, six-armed star-poly(ε-caprolactam) (Nylon-6).

Caprolactam and its analogous aminocaproic acid are called AB monomers be-
cause one end of their alkylene group is terminated with carboxy acid (A) and the
other with the basic amine (B) group. Linear chains created from AB monomers
generally terminate with A group on one end and B group on the other. Monomers
whose both ends are carboxy acid groups are referred to as AA monomers and
monomers whose both ends are amine or hydroxy groups are referred to as BB
monomers. In general, the AA and BB monomers do not react with themselves,
but only with each other. Linear chains made from equimolar amounts of AA and
BB monomers, are generally characterized by 50% of them each having one A
and one B end, 25% of the chains having two A ends and 25% having two B ends.
When in a reaction mixture containing AA and BB monomers are present highly
branched polymer species each containing both A and B end-groups or exclusively
A or B end-groups, the probability of crosslinking is greatly increased, followed
by the appearance of microgels and, finally, the appearance of "infinite" network
and gelation. An approach to minimize these undesired crosslinking reactions is
to perform the polycondensation reactions at high dilution, resulting in star-
polymers exclusively, or with only minute amounts of microgel impurities. In the
case of AB monomers, the situation is much easier to control. When the highly
branched polymer species are decorated by only one reactive group, either A or
B, then, at each growth stage only that reactive group will decorate all, or essentially
all growing segments of all star-polymers in the reaction medium. Hence, the
preparation of star-polymers by polycondensation of AB monomers may be con-
veniently carried out in solution at concentrations far higher than in the preparation
of star-polymers created by polycondensation of AA + BB monomers.

In two to be published articles we have described in some detail the preparation
of "Rigid Aromatic Fractal Polyamides"[8] and "Interpenetrating Blends of Rigid
Aromatic Fractal Polyamides and Nylon-6."[9] In the present article, certain aromatic
fractal polyamides (FPs), whose preparation and characteristics are discussed in
Reference 8, are used as the cores from which the flexible arms of star nylon-6
and star poly(ethyleneterephthalate) (PET) emanate. All the FPs used in the
present work are decorated with multiple reactive end-groups, onto which chains
of nylon-6 or PET are grafted or from which nylon-6 chains start growing by the
ring-opening polymerization of caprolactam. The preparation of the rigid FPs is
described in Reference 8 and will not be repeated here. The characterization results
of the FPs employed herein will be reported inasmuch as they relate to the present
work.

The star nylon-6 and star PET prepared herein are different from the usual star
polymers in several significant aspects: (a) these are products of polycondensation
and not polyaddition reactions; (b) the number of arms in each star polymer is
relatively small; (c) the length of the arms is far from being monodisperse and, in
fact, has a polydispersity, M_w/M_n, generally between 2 and 3; (d) the number of
arms per each core is not identical and is distributed about a characteristic average
number; (e) the aromatic FP cores of the star polymers are relatively large in size
and are highly porous in nature; (f) the nature of the polymers involved requires
the use of uncommon solvents with strong specific solvent-polymer attractive in-
teractions. All these deviations from the situations usually encountered in the

treatment of common star polymers make it impossible to directly compare them and to employ the common theoretical treatments to our star polymers. We, therefore, limit the discussion in the present paper to the synthesis of star nylon-6 and star PET and to some of their solution and solid-state properties.

EXPERIMENTAL

(a) Preparation of Rigid Fractal Polyamides

The general procedure for the preparation of rigid aromatic fractal polyamides (FPs) is described in detail in Reference 8 and will not be repeated here. Generally, we prepared fully aromatic rigid FPs, but in the present work, in order to increase the probability of chain grafting onto the FPs, the swivel-like half-aromatic and half-aliphatic diamine 4,4'-aminobenzylcyclohexylamine (ABCHA) was substituted in several instances for all or part of the stiff-linear fully aromatic 4,4'-diaminobenzanilide (DABA). As usual, the average length of the FP segments was controlled by the addition of p-aminobenzoic acid (PABA) and by the ratio of the difunctional monomers to the rigid trifunctional 1,3,5-benzenetricarboxylic acid (BTCA) serving as the branchpoint residue. The FPs in which ABCHA fully displaced DABA are listed in Table I. The low yields point to the fact that the Yamazaki polymerization[10] used in the preparation of FPs is far less efficient with aliphatic amines than with aromatic amines.[11] In such a case, the number of aliphatic amine end-groups in the FPs is expected to far exceed the number of aromatic amine end-groups. This, indeed, was found to be the case when solutions of the FPs in deuterated solvents were studied by means of ^{13}C-NMR as described later.

(b) Grafting of Nylon-6 Flexible Arms onto FPs

The grafting was conducted under two conditions, both using triphenylphosphite (TPP) as the grafting reagent. In the first, a solution of FPs with reactive end-

TABLE I

Fractal polyamides with only ABCHA diamine monomer

Sample code	Molar ratio ABCHA:BTCA:PABA	Yield,%	Intrinsic viscosity,dL/g.
A2560-21B	3:1:0	53	0.12
A2560-23A	5:2:0	55	0.13
A2560-23B	5:2:5	55	0.13
38326-14A	5:2:1	80	0.15
38326-14B	5:2:3	57	0.18
38326-14C	5:2:5	47	0.17
38326-14D	5:2:7	39	0.19
38326-14E	5:2:9	41	0.18

a) Intrinsic viscosities were measured at 25°C in N,N-dimethylacetamide.

groups was prepared in N,N-dimethylacetamide (DMAc). In a separate vessel, a solution of commercial grade nylon-6 with balanced number of amine and carboxy end-groups was prepared in DMAc/LiCl. The nylon-6 nicely dissolved in this solvent once the solution temperature reached ca. 130°C. The solutions were then thoroughly mixed and pyridine followed by TPP were added. The reaction was continued at around 115°C for not less than 3 hrs. To minimize gelation, the ratio of nylon-6 to FPs was kept very large, in the range of 98:2 by weight, and the solution rather dilute, at around 3% total polymer. Nevertheless, after several hours microgels usually appeared, especially when the FPs were created from AA and BB monomers but even in the case of AB-type monomers where essentially all the FP end-groups were amines. The gelation is most likely caused by the presence in the nylon-6 of chains with not only A and B ends but also with A and A or B and B ends. This solution procedure was repeated many times. In all instances where the graft-reaction was stopped before microgels made their appearance, a very uniform product was obtained.

When the grafting reaction was performed in the melt, rather rapid increase in the melt viscosity took place, followed by the appearance of microgels and, later, crosslinking. Here, nylon-6 and FP powders were thoroughly mixed with TPP at room temperature. The mixture was then passed at ca. 250°C through a Haake TW-100 twin-screw extruder. The residence time was about 3 min. and was sufficient for the graft-reaction to take place and gelation to occur. Microscopic observations indicated that not all the FPs dissolved in the molten nylon and small grains of the FPs remained suspended in the nylon matrix. These tended to clog the spinnerettes and prevented efficient melt-spinning of the melt-grafted system.

While the graft-reactions did take place both in solution and the melt as expected, the product quality was uncontrolled. With increased graft efficiency, microgels and macro-scale gel formation took place. This made the products obtained unsuitable for fiber melt spinning.

(c) Grafting of PET Flexible Arms onto FPs

PET was grafted onto reactive end-groups by a modification of the Yamazaki[10,11] procedure. During this work we have found that when amines served as the reactive end-groups of the FPs, the grafting did not proceed well. More reactive group was needed. In the case of PET grafting, we found that potassium carboxylate was such a group and when it was present the grafting reaction proceeded very well.

Potassium carboxylate terminated FPs (coded A2105-82G) were prepared in two steps. In the first, FPs (coded A2105-78B) characterized by intrinsic viscosity (I.V., [η]) of 0.17 and weight average molecular weight, M_w of 14,200, were prepared from monomer mixtures in which the molar ratio of carboxy acid to amine fell in the range of 1.05 to 1.10. The resulting FPs were very rich in carboxy end-groups, almost to the exclusion of free amines. After work-up and purification, the FPs were dissolved in DMAc. To this solution, ethanolic solution of KOH was added dropwise, with care being taken to precipitate the FPs as slow as possible, only after their carboxyl groups were neutralized to the potassium salt. The mixture was left overnight before filtration. After the solids were collected, they were washed several times with water and methanol and finally dried. Infrared scans revealed

that no free carboxy groups remained in the system. Element analysis showed the presence of about 8% potassium, consistent with all the carboxyl acid groups being converted to the corresponding potassium carboxylate.

To effect dissolution without degradation of PET, no LiCl may be tolerated in the solvent. The polymer requires, hence, a much higher dissolution temperature than nylon-6. Thus, PET was dissolved in N-methyl-2-pyrrolidinone (NMP) at about 190°C and the condensation reactions with amine-terminated FPs were conducted at about 185°C. The grafting was rather inefficient. Because of this we could obtain star PETs with no crosslinking and gelation, but with only two arms per star, on the average. Similar poor results were obtained when the grafting reaction was conducted in the melt. To overcome this the amine-terminated FPs were replaced by the potassium-carboxylate-terminated FPs described above, and a dramatic increase resulted in the average number of PET arms per star. A typical melt preparation procedure for star-PET follows: 60 g PET were ground and dried under dynamic vacuum at 130°C overnight. 0.6 g of the potassium-carboxylate-terminated FP (coded A2105-82G) were mixed with 0.91 g TPP. The mixture was added to the PET and thoroughly mixed in a sealed vessel. The well-mixed mixture was then melt blended in a Haake Rheocord-90 instrument for 20 min at 270°C with rotor speed of 50 rpm. At the end of each run the instrument was opened and the blended polymer collected and later characterized. Since the torque of the rotors of the Haake machine directly reflects the melt viscosity of the processed polymer, a comparison of the torques obtained from different samples under otherwise identical conditions, gives an indication of the melt viscosities and relative levels of grating of the PET onto the FPs. Results of intrinsic viscosities and, especially, light scattering measurements were consistent with the torque values. Typical results obtained on several star-PET are shown in Table IV.

(d)   Polymerization of Caprolactam as Flexible Nylon-6 Arms on FP Cores

The polymerization of caprolactam was conducted following a procedure of Sorenson and Campbell.[12] In a 500 ml three neck round bottom glass flask equipped with a distillation column, nitrogen inlet and outlet, a magnetic stirring egg and a controlled temperature oil bath, there were first melted 112 g of caprolactam and then dissolved 1 g of FPs under a slow nitrogen stream. The temperature was kept close to 250°C. Once the FPs fully dissolved in the molten caprolactam, either 2 g of water or 5 g of aminocaproic acid were added, the nitrogen stream stopped and the flask sealed. Because of the temperature, water tended to condense in the distillation column whose top was stoppered. When water was used as the initiator, the pressure was occasionally released to prevent explosions by allowing some of the water vapors to escape. No such precautions were needed when aminocaproic acid was used as the polymerization initiator. The reaction was allowed to continue under these conditions until the viscosity had significantly increased. Reaching this step typically took from 4 to 6 hours. Then, the nitrogen stream was renewed, which drove the water out of the system, allowing for condensation reactions to take place in addition to ring opening. The polymerization was allowed to continue for additional 1 to 3 hours, until the stirring egg could move no more. At that point the polymerization was terminated, the vessel cooled to room temperature and the

TABLE IV

Star-PET preparation in the melt[a]

Code	FP precursor	TPP, wt. %	Torque, m.g.	I.V., dL/g	M_w
PET blank	None	None	49	0.50	40,000
A1971-50B	None	1.5	98	0.52	43,000
A1971-55A	1% A2105-69A	None	47		
A1971-55B	1% A2105-72A	1.5	93		
A2105-82D	1% A2105-79B	None	41	0.47	
A1971-50C	1% A2105-78B	1.5	88	0.53	
A1971-50D	1% A2105-79B	1.5	57	0.50	
A2105-82K	1% A2105-82G	None	36	0.46	
A1971-50H	1% A2105-82G	1.5	259	0.65	169,000
A1971-53B	1% A2105-82G	1.5	435	0.84	150,000
A1971-53R	1% A2105-82G	1.5	404	0.74	120,000

(a) All melt processing was conducted at 270°C.

solid product obtained by breaking the flask. The product was placed in "dry ice" for 4 hours, after which it could be broken with a hammer and then ground in a Wiley mill. The ground material was heated under vacuum at 50 to 60°C for about 12 hrs in order to remove any water picked up during its handling. Some of the unreacted caprolactam sublimed off. The dry product was then washed in a litre of methanol which was then brought to boiling. The hot solution was filtered and the process repeated several times. Finally, the product was dried under dynamic vacuum at 100°C for 12 hrs.

The intrinsic viscosities of the extracted polymers, and the SEC characteristics of the star nylons are presented in Table VI together with the results of a linear nylon-6 (coded 38326-18) prepared in this study for comparison under conditions identical with the previous.

We attribute the consistently lower M_w obtained by SEC, relative to the results obtained by LALS and PCS, to two reasons: (a) Trifluoroethanol is a poorer solvent than formic acid for nylon[13] resulting in smaller size for the star-nylon molecules in this solvent, and (b) a minute fraction of microgels were observed by PCS in the star-nylons. These passed through the 200 nm filters used in sample preparation for LALS and were included in the resulting M_w. The same microgels were trapped by the SEC columns and were not included in the SEC M_w.

(e) Characterization Procedures

Proton and carbon-13 NMR spectra were obtained from solutions of the FPs and star polymers in deuterated solvents. The spectra were obtained at 50.3 and 100.6

TABLE VI

Star-nylon by caprolactam polymerization on FP cores[a]

Star-nylon	FP core	Initiator	I.V.	M_w,SEC	M_w,LALS	M_w,PCS	R_H,nm
38326-12B	A2560-23B	Water	1.31	39,000	52,000	–	–
38326-15	A2560-23B	Water	0.99	30,300	47,000	–	–
38326-16	A2560-23B	Water	1.64	66,900	95,000	–	–
38326-17R	A2560-23B	Water	1.28	55,100	81,000	–	–
38326-19	A2560-23B	Water	1.57	61,400	72,000	–	–
A2560-33A	A2639-10A	ACA	2.06	–	120,000	94,000	6.5
A2560-33B	A2639-10B	ACA	1.94	–	86,000	81,000	6.6
38326-18	None. Linear	Water	0.85	25,000	25,000	–	–

(a) All star-nylons contain 1 wt % FP cores. Water = 10 mol % water, ACA = 5 mol % aminocaproic acid. Weight average molecular weight, M_w, was measures intrifluoroethanol by SEC and in formic acid with 0.5M KCl by LALS and PCS. Intrinsic viscosity in m-cresol at 25°C.

Mhz in Varian XL-200 and Varian XL-400 Fourier transform NMR spectrometers. Dilute solution viscosities were measured in internal dilution Cannon-Ubbelohde glass viscometers with solvent efflux times longer than 100 s. The solvents used were DMAc, m-cresol, 0.5 M KCl in formic acid and, occasionally, conc. sulfuric acid. Weight average molecular weight, M_w, of the FPs and star polymers were measured on their filtered solutions in low-angle light scattering (LALS) Chromatix KMX-6 instrument. The hydrodynamic radius, R_H, and molecular weight distributions of the polymers were determined from diffusion measurements in a Langley-Ford LSA-II photon correlation spectrometer (PCS) by taking numerical transforms of the photon correlation data using an in-house enhanced version of Provencher's CONTIN program.[14]

Size exclusion chromatography (SEC) was performed on a Waters Associates 150C system with an internal Viscotek 150R viscosity detector and a LCD SpectroMonitor II UV detector set at 220 nm. The separation occurs at 35°C on a bank of two linear Phenogel[R] styrene-divinylbenzene columns with a solvent flow rate of 1 mL/min. The solvent was either trifluoroethanol with 0.1 M LiBr or NMP with 0.05 M LiBr. These solvents were also used for the light scattering and PCS measurements above. The SEC data were collected and analyzed with PE Nelson 2900 GPC software, version 4.05 for universal calibration and viscosity, and software developed at AlliedSignal Inc. to calculate hydrodynamic radii.

Wide-angle x-ray diffraction (WAXD) patterns were obtained from powdered

samples and from compression molded plaques in a Philips APD-3600 automatic diffractometer operating in parafocus mode and using copper radiation and diffracted beam monochromator. Optical microscopy studies at up to 400× magnification were conducted with an Olympus BH-2 polarized light microscope. Thermal scans were obtained from samples in nitrogen atmosphere using a duPont 9900 DSC instrument operating at 20K/min heating and cooling rates. Each sample was kept for at least 2 minutes at 270°C or higher between the heating and cooling cycles. All reported transitions are from the first cooling and second heating cycles.

RESULTS AND DISCUSSION

This is a first report on ongoing work involving star nylon-6 and star PET. Their novelty is due to the facts that both star polymers are obtained by polycondensation reactions and that the cores of the star polymers are relatively large, highly branched porous and rigid aromatic polyamides while the arms of the stars are flexible in nature. Data characteristic of the star polymers prepared herein are listed in Tables III, IV and VI. Characteristic data of the FPs used as cores in the preparation of the star polymers are tabulated in Tables I, II and V. Throughout the discussion below, it should be borne in mind that the amount of FPs in the star polymers listed in Tables III, IV and VI never surpassed 2 weight percent. The low level of

TABLE III

Star-nylon-6 prepared in solution from FPs and linear nylon-6[a]

Code of Star	Parent FP	M_w of Star by LALS	I.V. of Star dL/g	No. of Arms in star.
A2560-4A	A2105-74A	32,000	0.96	1
A2105-75A	A2105-72B	45,000	1.12	1.5
A2105-76A	A2105-72B	63,500	1.31	2
A2560-4C	A2105-74A	70,000	0.83	2
A2105-73B	A2105-72B	127,000	1.39	4
A2560-4B	A2105-74A	128,000	1.51	4
A2560-4D	A2105-74A	220,000	1.52	7
A2105-71A	A2105-69A	300,000	1.75	9
A2560-4E	A2105-74A	340,000	2.04	10

(a) All arms of star polymers were made from linear nylon-6 LSL grade,

M_w = 33,200. The concentration of FPs in the star polymers was

1% by weight.

TABLE II

FPs used in solution preparation of star nylon-6[a]

FP Code	M_w of FP	Intrinsic Viscosity of FP, dL/g	R_H, nm
A2105–69A	46800	0.32	3.2
A2105–72B	22400	0.17	2.0
A2105–74A	23000	0.18	2.2

(a) Star polymers made from FPs and nylon-6 LSL grade, M_w = 33200.

TABLE V

FPs used for caprolactam polymerization

FP code	I.V., dL/g	M_w	R_H, nm
A2560–23B	0.13	11,800	~1.3
A2639–10A	0.28	63,000	3.2
A2639–10B	0.20	23,000	1.6

FPs used throughout was in order to prevent, or at worse minimize, the appearance of microgels in the star polymers.

The results in Tables III, IV and VI clearly show that, under auspicious conditions, star nylon-6 and star PET can be prepared with appropriate FPs as cores. It is obvious that comparable dendrimers may serve as well as cores for polycondensation (and polyaddition) star polymers. The same tables indicate, however, that *control* of the number of arms per star could not be attained under our reaction conditions and limited number of grafting reactions, and may not be attainable at all. Below, this point will be revisited by us.

Several interesting observations were made during the polymerizations and characterizations. Viscosity measurements conducted in a SEC instrument in conjunction with molecular size (weight) determinations of star nylon-6 revealed a unimodal molecular weight distribution (MWD) and a power dependence of the intrinsic viscosity (I.V., [η]) on molecular weight far lower than in the case of linear nylon-6. This is clearly evident from Figure 1. In the various samples of star nylon studied by SEC, there were no hints of either bimodal MWD or the presence of linear nylon, which will force the I.V.—molecular weight power dependence plots to show a curvature that may imply the coexistence of linear and star nylon-6 in the same sample. The SEC results are consistent with those of PCS, typified by the scans in Figures 2 and 3, where the main peak, corresponding to around 98% of the sampled polymer, shows a unimodal MWD shape. The minority material, of 1 to 2% by weight, is of very high molecular weight, evidently a microgel in nature.
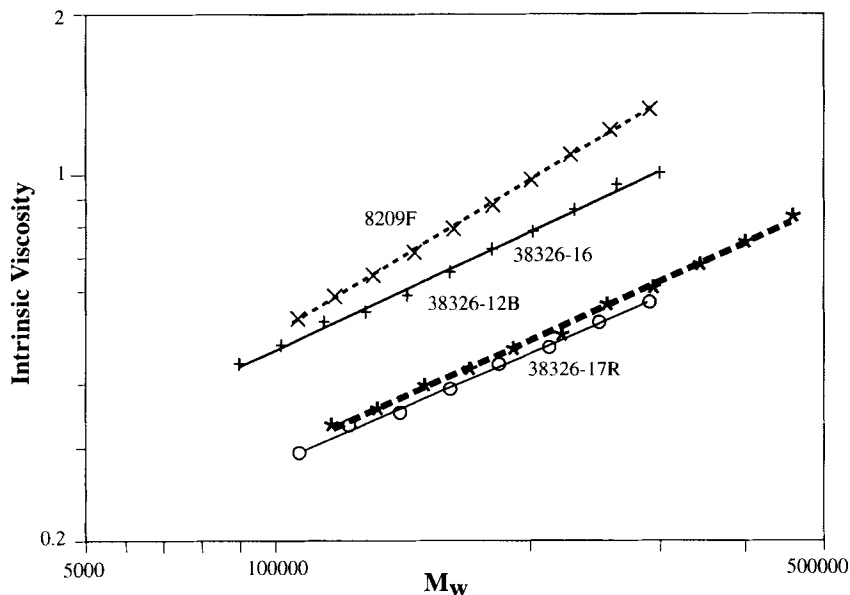
FIGURE 1   Mark-Houwink plot of 3 star nylon-6 and one linear nylon-6, I.V. *vs.* M_w.
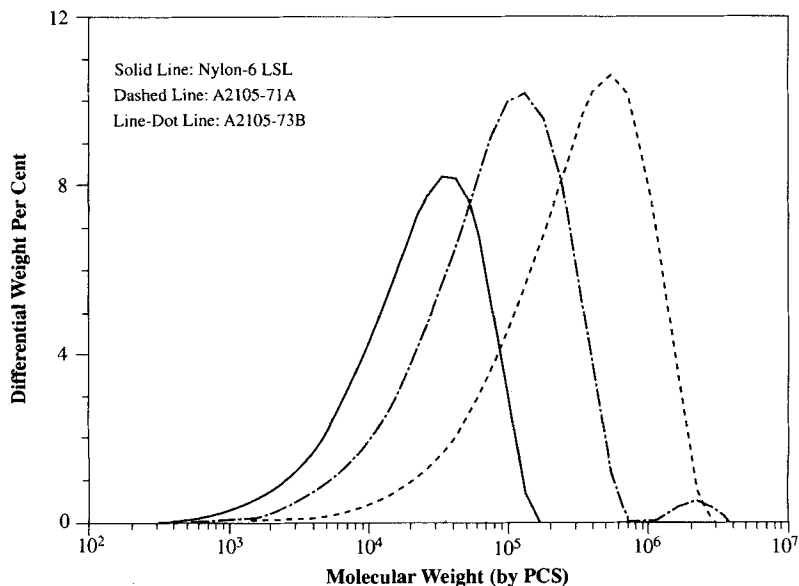

FIGURE 2   Molecular weights by PCS of two star nylons and one linear nylon blank.

A more important observation is that there is no indication of bimodality on the low molecular weight part of the distributions in all the SEC and PCS scans, a location where the linear nylon-6 is expected to be found if it were present in the investigated systems.

Another interesting observation is the following: During the polymerization of
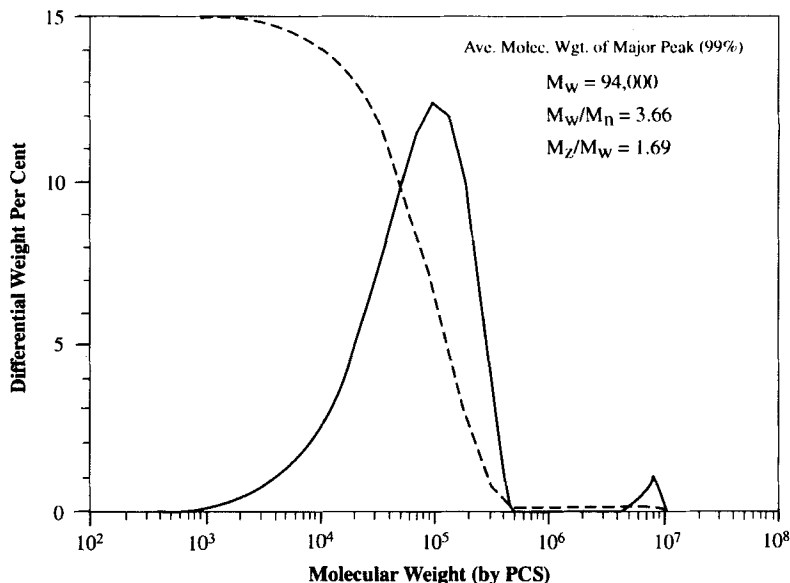
FIGURE 3 Molecular weight distribution of A2560-33A by PCS.

star nylon from caprolactam we repeatedly performed exhaustive fractionation using trifluoroethanol (TFE) at room temperature. We were surprised to find that when polymerization did take place, it almost exclusively ended up as star nylon. Except for caprolactam monomer and 1–2% nylon oligomer, all the polymerized caprolactam ended up as flexible nylon arms of star nylon polymers. It is important to emphasize in this context that the polymerization took place only when water or aminocaproic acid were present in the system as polymerization initiators. In their absence no caprolactam polymerization took place under otherwise identical conditions, and at the end of the runs it was easy to recover the unreacted FPs and the caprolactam monomer by simply dissolving the reaction mixture in warm water, methanol or acetone.

The power dependence of $[\eta]$ on M_w is generally written in the form of a Mark-Houwink equation

$$[\eta] = KM_w^a$$

where K is a constant characteristic of each polymer-solvent system. From Figure 1 we determined the value of a for 3 star nylon polymers to be $a = 0.59$ for 38326-17R, $a = 0.63$ for 38326-12B and $a = 0.64$ for 38326-16. These three star nylons were prepared by caprolactam polymerization and were carefully washed prior to testing to remove residual monomer. For comparison, the commercial grade Capron 8209F of linear nylon-6 was subjected to the same purification and test procedures with the result of $a = 0.83$. The high value of a for the linear polymer, and the low values of a for the three star polymers are all consistent with expectations.

It was mentioned previously that we could only coarsely control the number of

flexible nylon or PET chains grafted onto each FP to create star polymers. There are several possible reasons for this. Among them one may mention the low efficiency of the grafting reaction, and the facts that the size of the FPs and the number of end groups per FP, as well as the ratio of amine to carboxy end groups especially in FPs prepared from AA and BB monomers were not well controlled. When the FPs were created from the more expensive AB and AB_2 monomers, then, by having a majority of B end groups in the reaction mixture, we could easily insure that all, or practically all, the end groups were amines. By reversing the ratio through the use of AB + A_2B monomers, we could insure that all the end groups will be carboxy acids. By running repeat FP polymerization experiments, one can determine the reaction conditions necessary to produce a desired molecular weight and number of end groups per FP, and gain a substantial control over the number of arms of the star polymer progeny even with the low efficiency of the grafting reaction. So, by first refining the polymerization conditions of the FPs and by the judicious choice of the appropriate comonomers, one may obtain FPs of a desired molecular weight, number of end groups, and control over the ratio of amine to carboxy end groups. Such extensive series of experiments was beyond our means but may be tried by others in the future.

When the FPs were created from the cheaper AA + BB monomers with A_3 branchpoints, the results were far harder to control. In this case, we were confronted not only with the lack of repeat experiments needed to control the molecular weight and total number of end groups per FP, but the nature of the end groups was poorly controlled. Here, the use of AA and BB monomers resulted in the end groups population to contain both carboxy acids and amines. The ratio of acid to amine could be controlled to some extent by the ratio of A to B groups in the monomer feed, but as the ratio of A/B increasingly deviated from 1.00, the total yield of the FP product and their M_w dramatically decreased. Because of constraints imposed on us when using AA + BB monomers, we ended up with decent yields of FPs whose M_w's are shown above and whose A/B ratios fell in the range from 0.5 to 2.0. All these reflected themselves in low grafting efficiency of both nylon-6 and PET chains on the FPs.

Another important reason for the small number of grafted arms per star is the fact that grafted chains slowed or prevented the reactive ends of ungrafted chains from reaching reactable sites in the FP neighborhood of the grafted chain. The picture in Figure 4 is a computer simulation with energy minimization[15] of one nylon-6 chain grafted onto one FP. Their sizes are comparable to the respective nylon and FP polymers actually used in the grafting procedure. From the Figure it is not hard to extrapolate and find that when there are about 10 nylon chains grafted onto each FP, its exterior with the reactive end groups are shielded by the grafted chains, greatly reducing the probability of additional grafting. We believe that this may be one of the reasons we could graft on each FP no more than 10 flexible arms.

The number and length of nylon arms growing from reactive sites on FPs by caprolactam polymerization are not known to us at present. From the highest molecular weights obtained by caprolactam polymerization, in Table VI, we estimate that a large fraction of the reactive groups on the FPs were consumed by
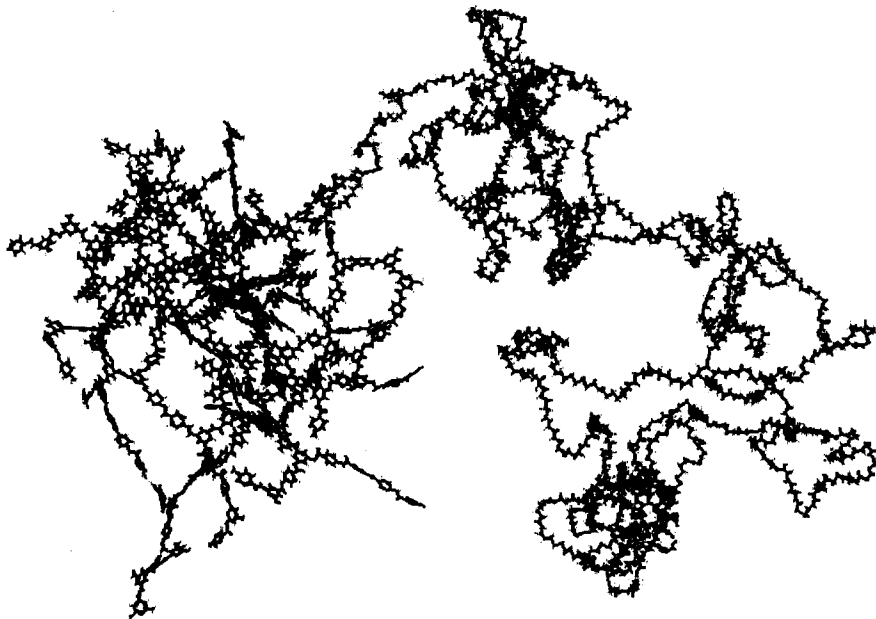
FIGURE 4   One nylon-6 chain attached to a rigid aromatic FP. Molecular weights: 28250 g/mol for nylon chain, and 26000 g/mol for FP.

serving as the points of origin of the growing nylon arms. At present, however, we cannot determine the exact magnitude of this fraction.

In conclusion, this initial report on condensation star polymers with FP cores shows that nylon-6 and PET flexible arms of star polymers can be created by two techniques: grafting pre-existing chains onto reactive sites on the exterior of rigid FP cores, and growing nylon-6 arms by polymerizing caprolactam to form arms originating from reactive sites on the FPs. At present the number of arms per star and their length are not controlled. Much more future experimental work is needed in order to learn how to control both these parameters.

References

1. B. J. Bauer, L. J. Fetters, W. W. Graessley, N. Hadjichristidis and G. F. Quack, *Macromolecules*, **22**, 2337 (1989).
2. A. T. Boothroyd, G. L. Squires, L. J. Fetters, A. R. Rennie, J. C. Horton and A. M. B. G. de Vallera, *Macromolecules*, **22**, 3130 (1989).
3. A. T. Boothroyd and L. J. Fetters, *Macromolecules*, **24**, 5215 (1991).
4. L. J. Fetters, A. D. Kiss, D. S. Pearson, G. F. Quack and F. J. Vitus, *Macromolecules*, **26**, 647 (1993).
5. G. Allegra and F. Ganazzoli, *Prog. Polym. Sci.*, **16**, 463 (1991).
6. J. W. Mays and N. Hadjichristidis, *J. Appl. Polymer Sci. Appl. Polym. Symp.*, **51**, 55 (1992).
7. J. M. Warakomski, *Chem. Mater.*, **4**, 1000 (1992).
8. S. M. Aharoni, "Rigid Aromatic Fractal Polyamides," manuscript submitted for publication (1995).
9. S. M. Aharoni, "Interpenetrating Blends of Rigid Aromatic Fractal Polyamides and Nylon-6," manuscript submitted for publication (1995).
10. N. Yamazaki, M. Matsumoto and F. Higashi, *J. Polymer Sci. Polym. Chem. Ed.*, **13**, 1373 (1975).

11. S. M. Aharoni, *Intern. J. Polymeric Mater.*, **26**, 9 (1994).
12. W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," 2nd. ed. Wiley-Interscience, New York, 1968, p. 344.
13. S. M. Aharoni, F. G. Cilurso and J. M. Hanrahan, *J. Appl. Polymer. Sci.*, **30**, 2505 (1985).
14. S. W. Provencher, *Comput. Phys. Commun.*, **27**, 213, 229 (1982).
15. Generated by Dr. W. B. Hammond on August 29, 1992, using POLYGRAPH[R] program with energy minimization.