based on the MSVD technique is overestimated. In the molecular weight range 2.89×10^4–$\sim 4.4 \times 10^4$, the polydispersity, M_w/M_n, is around 1.7–1.8 according to the MWD based on the CONTIN method. Our CONTIN results agree with the GPC analysis on similar PBA samples in DMAC with 4 wt % LiCl, as reported by Schaefgen.[14] Both methods (light scattering and GPC) showed M_w/M_n is around 1.7–1.8 for PBA samples of $M_w > 1 \times 10^4$.

In summary, we found a larger persistence length, a higher α_D (thus higher α_η) value, and a higher molecular anisotropy value for PBA in DMAC with 3% (g/mL) LiCl than those of PPTA in concentrated sulfuric acid. Thus, the PBA chain is more rigid than the PPTA chain. The experimentally measured C^+ values are close to C^{**} (eq 18) values for all PBA samples studied. The measured self-beating net autocorrelation functions have been analyzed by using the cumulants technique and the MSVD and CONTIN methods. MWD results from different methods of data analysis are compared. For unimodel distributions both MSVD and CONTIN methods are reliable. For bimodal distributions, the CONTIN method is more reliable.

With recent advances in photon correlation spectroscopy and Laplace inversion methods, laser light scattering characterization of polymer molecular weight distributions is within reach as a routine technique for hard to characterize speciality polymers.

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Registry No. PBA (SRU), 24991-08-0; PBA (homopolymer), 25136-77-0.

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Dilute and Concentrated Solution Properties of Zigzag Polymers Comprising Long Rodlike Segments with Freely Rotating Joints

Shaul M. Aharoni

Engineered Materials Sector Laboratories, Allied Corporation, Morristown, New Jersey 07960. *Received May 29, 1986*

ABSTRACT: Nine fully aromatic, highly regular "zigzag" polyamides and poly(ester amides) were prepared, each consisting of identical virtual bonds with freely rotating joints joining them along the chain. The length l_0 of the virtual bonds ranged from 10.6 Å up to 44.7 Å. In dilute solutions the behavior of the zigzag polymers is dictated by their freely rotating joints, with their rodlike segments acting as long virtual bonds in freely rotating random coils. The poly(ester amides) behave as highly draining coils, while the polyamides are nondraining. The size of the zigzag polymer coils is clearly dependent on l_0. Their Kuhn segment length A approximates three virtual bonds. In concentrated solutions the solution behavior is dominated by M_w and C and to a lesser extent by l_0. The effect of the virtual bond length is especially noticeable when the viscosity is normalized to remove the effects of differences in chain length. At very high concentrations the zigzag polymers do not form lyotropic liquid crystals despite the fact that their rodlike segments are of sufficient length to form anisotropic solutions. In the bulk, the zigzag polymers do not form thermotropic liquid crystals. A chemically similar rodlike poly(ester amide) forms both lyotropic and thermotropic liquid crystals. The density of the semicrystalline zigzag polyamides and, especially, the amorphous zigzag poly(ester amides) indicates that the polymeric chains are packed just as well as in other polymers with much shorter l_0.

Introduction

Solution properties of polymers are generally treated in terms of three models: the flexible Gaussian coil, the rigid rod, and the semiflexible molecule whose flexibility is due to a gradual accumulation of the effects of small thermal vibrations of valence angles, bonds, etc.[1] Such semiflexible chains are commonly treated by the persistent coil model of Kratky and Porod[2] or by the helical wormlike chain model of Yamakawa.[3-5] Another group of semiflexible polymers is the one whose flexibility is a consequence of relatively easy transitions between several rotational isomers. Such polymers will be the focus of the present study. The chains of each of the rotational isomeric semiflexible polymers in this work are represented by a sequence of identical rodlike segments, each characterized by a virtual bond of length l_0 and a diameter d. The rodlike segments are joined together by essentially freely rotating joints. The polymers in this study can be visualized, hence, as

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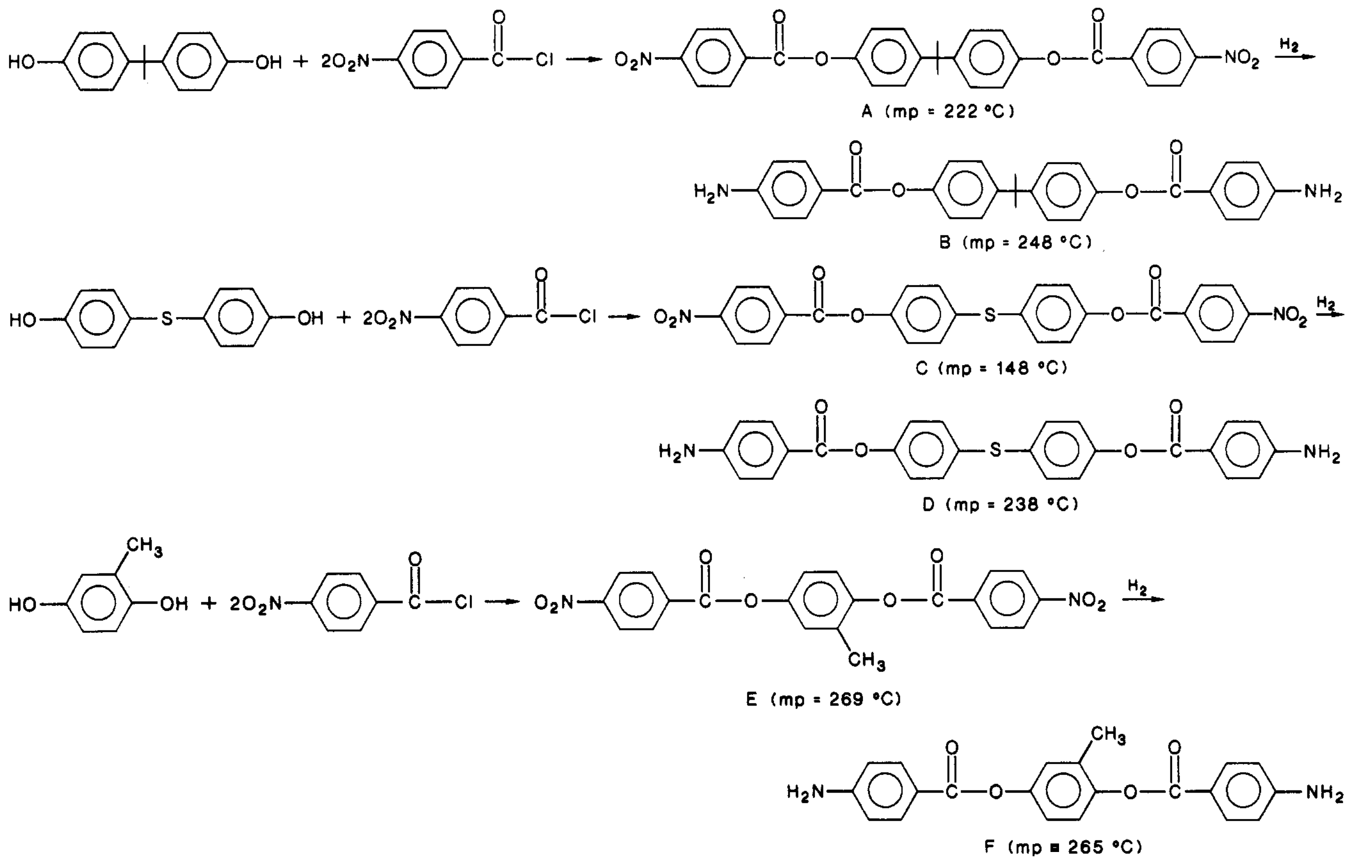
Scheme I



A (mp = 222 °C)

B (mp = 248 °C)

C (mp = 148 °C)

D (mp = 238 °C)

E (mp = 269 °C)

F (mp = 265 °C)

freely rotating polymers whose $l_0 \gg d$. Furthermore, in our case, the Kuhn segment length, A, is several times longer than the virtual bond length l_0. This is unlike the common freely rotating chains where $A \propto d$ ($A = 2d$, to be exact),[6] and the Kuhn segment length is much larger than l_0.[7] When limited to two dimensions, our polymers assume a "zigzag" shape and will be therefore referred to as zigzag polymers throughout this work.

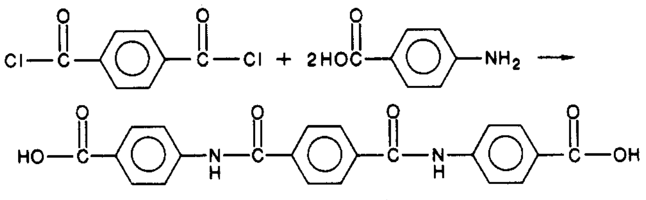
There exist in the literature only very few references[8-12] to aromatic, semiflexible, zigzag, or close to zigzag polymers having more than a single aromatic ring per virtual bond and where the structure along the chain is fully regular and at least some solution properties are given. The available data are too scarce to allow a determination of whether the length l_0 affects the solution properties of aromatic semiflexible polymers consisting of long rodlike segments and flexible freely rotating joints. In order to determine the effects of the length l_0 on the solution behavior of aromatic semiflexible chains, we have synthesized in this work zigzag polyamides and poly(ester amides) with virtual bonds spanning two to seven aromatic rings. The method of preparation allowed a careful control of the virtual bond length and placement, ensuring that each polymer comprises identical virtual bonds all along the chain. The bulk of this work is a study relating the dilute and concentrated solution behavior of polymers having freely rotating joints to the length of the rodlike segments between these joints.

Experimental Section

A. Synthesis of Monomers and Zigzag Polymers. Several of the monomers subsequently used in the polymerizations were prepared in two steps (Scheme I). In the first, a classic Schotten–Baumann single-phase reaction, using cold 1,2-dichloroethane as solvent and pyridine as an acid acceptor, was used to condense dihydroxy species with *p*-nitrobenzoyl chloride. In the second step, the purified product was hydrogenated over Raney nickel in an autoclave under 8 atm of hydrogen pressure.

Depending on the solubility of the arylene bis(nitrobenzoate) species, the hydrogenation was carried in *N*,*N*-dimethylformamide (DMF) or *N*,*N*-dimethylacetamide (DMAc) at the lowest temperature in which a 10 wt/vol % solution could be maintained. After the hydrogen consumption ceased, the reaction mixture was removed from the autoclave, filtered hot to remove the catalyst, and allowed to cool. A tenfold volume of added methanol usually precipitated the desired arylene bis(aminobenzoate) in reasonable purity. Recrystallization from hot methanol or 10:1 methanol/DMF mixture was often required in order to obtain monomers of purity sufficient for polymerization. It should be noted that, while products B and F were obtained in yields of about 75%, the hydrogenation of C to D resulted in yields of less then 50% and a contamination of the catalyst by several nickel–sulfur compounds.

An additional, dicarboxy-terminated monomer was prepared by the Schotten–Baumann procedure:



G (mp = 377 °C)

This monomer was subsequently polymerized with monomer B to produce a poly(ester amide) with seven para-linked aromatic rings in each rodlike segment between the freely rotating joints.

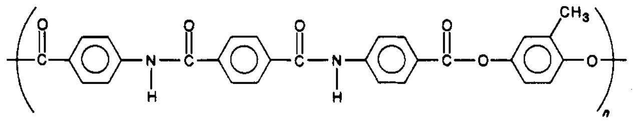
Monomers obtained from chemical supply houses were 4,4′-dicarboxyphenyl ether, 4,4′-diaminophenyl ether, 4,4′-dihydroxyphenyl sulfide, 4,4′-dihydroxyphenylisopropylidene (bisphenol A), *p*-phenylenediamine, 4,4′-diaminobenzanilide, methylhydroquinone, and nitroterephthalic acid. 2,6-Naphthalenedicarboxylic acid was prepared in our laboratories by hydrolysis of the corresponding dimethyl ester.

Polymerizations were carried out at about 100 °C in 5% solutions of LiCl in DMAc (DMAc/5% LiCl) in the presence of triphenyl phosphite and pyridine. The monomer charge was about

10 wt/vol % based on the combined volume of the DMAc/5% LiCl and pyridine. This procedure is known as the Yamazaki procedure[13] and is described in detail in ref 14. The polymerizations were usually continued for 3 h, with essentially 100% yield. The polymers were precipitated in excess methanol, filtered, washed in water and then methanol again, and finally dried in a vacuum oven at >100 °C to constant weight.

B. Synthesis of Fully Aromatic Rodlike Poly(ester amide). It is well-known[15] that para-substituted fully aromatic polyamide and polyester chains behave as substantially rodlike entities. The high extension of these macromolecules is maintained even when additional substituents, such as halogen, alkoxy, or alkyl groups, are attached to the aromatic rings along the chain.[15] Because of their chain rigidity and extension, these polymers exhibit liquid crystalline mesophases in molten bulk and/or concentrated solution. The high extension of, at least, the aromatic polyamides carries deep into the highly dilute solution regime, as repeatedly verified by light scattering and viscosity studies.[16-20]

In order to calculate the length of the virtual bonds and evaluate the segmental rigidity in solution of our zigzag poly(ester amide) polymers, one must know whether the ester and amide groups in them are all extended in the trans conformation, as is the case for rodlike polyaromatics. It was believed that if a rodlike aromatic poly(ester amide) is prepared and found to be liquid crystalline at elevated temperatures and, preferably, in solution at ambient temperature we can then safely assume that essentially all its amide and ester groups are extended in the trans conformation[15] and that this is most likely the preferred conformation of these groups in our zigzag polymers. Therefore, an aromatic poly(ester amide) of the structure



was synthesized in two steps from terephthaloyl chloride, *p*-aminobenzoic acid, and methylhydroquinone. The first step was a single-phase Schotten–Baumann procedure, followed by the Higashi procedure,[21,22] a direct polycondensation in the presence of diphenyl chlorophosphate and pyridine. The resulting poly(ester amide) had an intrinsic viscosity of 0.61 dL/g in DMAc/5% LiCl. The polymer showed lyotropic liquid crystallinity in solvents such as H_2SO_4, as well as apparent thermotropic mesomorphicity above about 360 °C. This behavior indicated that the trans conformation of both ester and amide groups along the same chain is maintained even in solution, allowing us to calculate the length of the rigid segments in the zigzag polymers accordingly.

C. Characterization. The structures of all monomers and polymers prepared in this work were confirmed by ^{13}C NMR spectra obtained with a Varian XL-200 Fourier transform NMR spectrometer from solutions in deuteriated DMAc or Me_2SO. Monomer purity was evaluated by integrating the resonance peaks of the desired product and the impurities. Infrared (IR) spectra were obtained from the polymers in KBr pellets by using Nicolet 170SX and Perkin-Elmer Model 283B spectrophotometers. In all cases the pulverized polymer and KBr were dried for 8 h or longer in a high vacuum at 150 °C. Thermal data were obtained with a Du Pont 9900 differential scanning calorimeter (DSC) instrument at a heating rate of 20 K/min in nitrogen atmosphere. Thermogravimetric analysis (TGA) was conducted in a Du Pont instrument in argon atmosphere, with a heating rate of 10 K/min up to 700 °C. Microscopy studies using cross-polarized light were conducted with an Olympus BH-2 microscope equipped with a Reichert hot stage capable of reaching about 385 °C and a Zeiss Ortholux microscope equipped with a hot stage reaching up to 360 °C.

All viscosities were measured at 25 °C. Intrinsic viscosities were measured in internal dilution Cannon–Ubbelohde glass viscometers. Most such measurements were conducted in DMAc/5% LiCl solutions and some in DMF. High-concentration viscosities in DMAc/5% LiCl were measured in large bore glass viscometers and in a Nametre direct readout viscometer in which the sphere oscillates at a natural frequency of 4060 Hz. The viscosities, in centipoise (cP), obtained by both procedures were very close to each other. The flow rate in the glass viscometers was sufficiently slow for the measured viscosities to approximate η_0, the zero-shear viscosity. The solvent viscosity, η_s, of DMAc/5% LiCl at 25 °C was measured to be 2.39 ± 0.05 cP.

Wide-angle X-ray diffraction (WAXD) patterns were obtained from the powdered polymers in a Philips diffractometer operating in parafocus mode with monochromatized copper Kα radiation.

Weight-average molecular weights, M_w, were measured by low-angle laser light scattering using a Chromatix KMX-6 instrument. Hydrodynamic radii, R_H, were determined by photon correlation spectroscopy (PCS) in a Langley–Ford multiangle photon correlation instrument. Because of the relatively low scattering intensity and small size of the studied polymers, the PCS correlation functions exhibited a level of noise necessitating the use of a multiexponential fit (DISCRETE) program to obtain reliable statistics. In most cases, two exponentials described the data well. Depending on molecular weight, the data were obtained from 0.4–1.0% solutions of the polymers in DMAc/5% LiCl at 25 °C. Static light scattering studies were performed in a C. N. Wood light scattering monophotometer Model 6000. The results were found to be at the threshold of resolution, indicating the radius of gyration, R_G, of our polymers to be in the range of 100 Å or smaller. Dissymmetry studies were conducted in the same instrument, leading to the same conclusions.

Specimens for density measurements were prepared from the finely ground polymers at pressures of 1.25 and 1.62 GPa and at ambient and 200 °C mold temperatures. No difference in the results was observed as a function of mold pressure, and only slight differences due to temperature changes were observed. The results of three or more specimens were averaged to give the reported values. The densities of the polymers were determined by pycnometry in 1,2-dichloroethane mixtures with either methanol or carbon tetrachloride.

D. Calculations of Structural Parameters. The polymers described in this work consist of long rodlike segments connected by flexible swivels or joints. These segments are rather rigid and comprise up to seven para-substituted aromatic rings linked together by amide or ester groups in their trans conformation. The swivels, made of –O–, –S–, and $-C(CH_3)_2-$ groups, are not freely jointed but allow rather high levels of torsional rotation[23,24] about the long virtual bonds. The length l_0 of the virtual bonds, the angle θ between them, and the projected bond length $l_0 \sin(\theta/2)$ were calculated from the data of Tonelli,[23,25] Jones et al.,[26] and Flory and associates.[27-29] By definition, the chain contour length L is Nl_0. The extended chain end-to-end distance, L_w, is $Nl_0 \sin(\theta/2)$, where N is the number of virtual bonds in the chain.

Theoretical estimates of the radius of gyration, R_G, are available for several models. For the classical Gaussian freely jointed chains[30]

$$R_{G_g} = l_0(N/6)^{1/2} \tag{1}$$

For the freely rotating chain of large N and a single fixed angle θ, the radius of gyration is

$$R_{Gfr} = [(N/6)l_0^2(1 - \cos\theta)/(1 + \cos\theta)]^{1/2} \tag{2a}$$

$$R_{Gfr} = R_{Gg}[(1 - \cos\theta)/(1 + \cos\theta)]^{1/2} \tag{2b}$$

In the case of our polymers, the fixed angles between the virtual bonds are 110° for the sulfide, 112° for bisphenol A, and 119° for the ether joints.[23-29] These angles place the values of R_{Gfr} in the range $1.414R_{Gg} < R_{Gfr} \lesssim 1.732R_{Gg}$. A third model is the wormlike coil model of Yamakawa. Defining the persistence length, q, as $q = A/2$, one obtains the wormlike model radius of gyration, R_{Gw} from[31]

$$R_{Gw} = [(Lq/3) - q^2 + (2q^3/L) - (2q^4/L^2)(1 - e^{-L/q})]^{1/2} \tag{3}$$

For chains with $L/q \gg 1$, the general relationship[32]

$$6R_G/L = 2q[1 - (L/q)^{-1}] \tag{4}$$

holds, and from this one obtains

$$A = 2q = 6R_G^2/L \tag{5}$$

Experimental estimates of the radius of gyration are obtained from intrinsic viscosity, $[\eta]$, measurements

$$R_{\mathrm{Gvisc}} = ([\eta]M/6^{3/2}\phi_\infty)^{1/3} \qquad (6)$$

where M is the molecular weight and $\phi_\infty = 2.68 \times 10^{21}$ when the viscosity is measured in units of deciliters per gram is Flory's universal constant.[33] In his treatment of polymer solution viscosity, it was shown by Tanford[34] that the radius of gyration for freely draining coils can be closely approximated from measured values of $[\eta]$, M, and the hydrodynamic radius, R_{H}

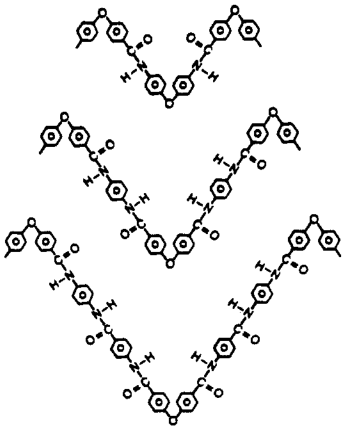
$$R_{\mathrm{Gfd}} = (M[\eta]/\pi N_{\mathrm{a}} R_{\mathrm{H}})^{1/2} \qquad (7)$$

where N_{a} is Avogadro's number. The radius of gyration for nondraining coils can be approximated from that of draining coils by the use of the following relationship:[34]

$$R_{\mathrm{Gnd}} = R_{\mathrm{Gfd}}/(3.3)^{1/2} \qquad (8)$$

Results and Discussion

Three aromatic polyamides and six aromatic poly(ester amides) were prepared by polymerization procedures requiring heating not higher than about 100 °C. Their NMR-confirmed structures are all shown below. The polymers are encoded according to the length of their virtual bond and its nature. Thus, the polyamides having 2, 3, and 4 aromatic rings per virtual bond are denoted by 1a, 1b, and 1c, respectively. Similarly, the poly(ester amides) with 3–7 rings per virtual bond are denoted by 2a–2f, respectively. It is important to recognize that in no case did the polymerization reaction involve the freely rotating joints or the preformed ester groups. This resulted in all the polymers having well-defined zigzag structures with virtual bonds of identical length for each polymer. These highly regular structures stand in contradistinction to the irregular structures one obtains from high-temperature melt polymerization. This irregularity appears to be the case in some fully aromatic[35] and aromatic–aliphatic[36] poly(ester amides) recently reported in the literature.



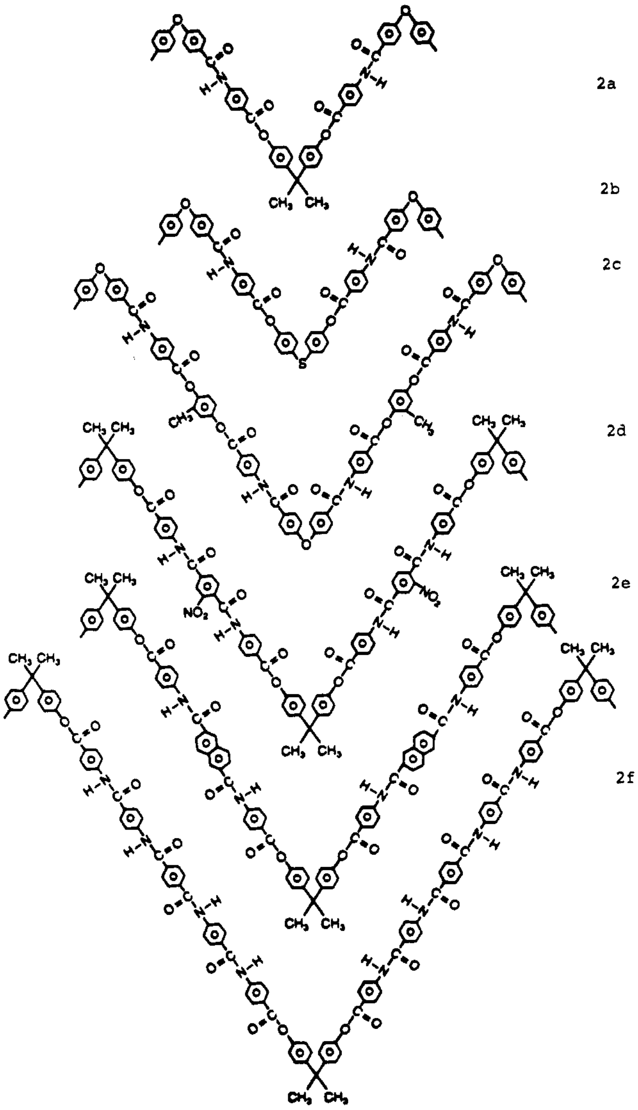
1a

1b

1c

Dilute Solution Regime. Dilute solution properties of all the zigzag polymers in DMAc/5% LiCl, including experimentally determined weight-average molecular weight, M_{w}, hydrodynamic radius, R_{H}, and intrinsic viscosity, $[\eta]$, are listed in Table I. In addition to the experimental results, the table contains values of radii of gyration obtained by the use of the different models as well as virtual bond length l_0, number of such bonds per chain, N, and Kuhn segment length, A. Also tabulated is the projected chain end-to-end distance, L_{w}, defined above. The values of A, obtained from R_{Gfd} by the use of eq 5, turned out to be rather large in the case of the polyamides, but are reasonably close to $A = 3l_0$ for the poly(ester amides). The reasons for the scatter in the A values of the 2f family are not fully understood at present.

A glance at Table I reveals that the intrinsic viscosities of the zigzag polyamides are of magnitudes typically observed for common random coil polyamides of similar molecular weights, such as poly(ϵ-caprolactam).[37] The intrinsic viscosities encountered among common polyamides are substantially larger than those observed for polyesters of comparable molecular weight. The high intrinsic viscosities obtained from common flexible polyamides reflect, we believe, the strong interactions between the polymer and solvent, leading to coil expansion. In the case of the zigzag polyamides, no polyelectrolyte effect was observed upon dilution during the viscosity measurements. However, the freely rotating nature of the zigzag polyamides and the interactions with the solvent are expected to produce by themselves rather expanded coils. Therefore, it is not surprising that the expanded coils of our zigzag polyamides will be of relatively similar sizes as the coils of common flexible polyamides.



2a

2b

2c

2d

2e

2f

The intrinsic viscosities of the zigzag poly(ester amides) are about twice the magnitude observed for flexible polyesters of similar molecular weights, such as poly(ethylene terephthalate).[38] We believe this to reflect the expanded coil nature of the freely rotating zigzag chains. At the same time, despite the high solubility in DMAc/5% LiCl and the high absolute values of $[\eta]$, the zigzag poly(ester amides) show a very weak power dependence of $[\eta]$ on M_{w}. Thus, the four members of the 2a family follow the relationship

$$[\eta] = 6.96 \times 10^{-3} M_{\mathrm{w}}^{0.419} \qquad r = 0.999$$

while the seven members of the 2f family obey

$$[\eta] = 4.66 \times 10^{-3} M_{\mathrm{w}}^{0.507} \qquad r = 0.969$$

Table I
Zigzag Polymers and Their Dilute Solution Properties[a]

polymer	M_w	$[\eta]$, dL/g	L_w	l_0	N	A	R_H	R_{Gvisc}	R_{Gg}	R_{Gfr}	R_{Gfd}	R_H/R_{Gfr}	R_H/R_{Gfd}	R_{Gfr}^2/M_w	R_{Gfd}^2/M_w
Polyamides															
1a	24000	0.98	1125	10.64	114	96.70	59	84.2	46.4	78.7	145.2	0.75	0.41	0.258	0.878
1b	18000	0.76	810	17.14	55	102.42	45	70.3	51.9	89.9	126.8	0.50	0.35	0.449	0.893
1c	22000	0.90	1000	23.64	49	103.90	52	79.5	67.6	117.1	141.9	0.44	0.37	0.623	0.915
Poly(ester amides)															
2a1	8600	0.31	390	18.61	25	49.49	37	40.7	38.0	60.2	61.7	0.61	0.60	0.421	0.443
2a2	10200	0.335	470	18.61	30	52.70	37	44.3	41.6	65.9	69.9	0.56	0.53	0.426	0.479
2a3	13000	0.37	600	18.61	38	55.16	38	49.6	46.8	74.1	80.8	0.53	0.47	0.422	0.502
2a4	16700	0.41	770	18.61	49	55.49	43	55.8	53.2	84.3	91.8	0.51	0.47	0.426	0.505
2b	6100	0.30	285	18.82	18	55.26	31	35.9	32.6	50.4	55.9	0.62	0.55	0.365	0.512
2c	32200	0.90	1480	31.38	55	83.65	64	91.7	95.0	164.5	154.9	0.39	0.41	0.840	0.745
2d	16000	0.32	660	31.72	25	47.57	43	50.6	64.7	95.9	79.4	0.45	0.54	0.575	0.394
2e1	10000	0.45	440	34.44	15.5			48.5	55.4	82.1				0.674	
2e2	13200	0.52	585	34.44	20.4	70.34	44	55.8	63.7	94.4	90.9	0.47	0.48	0.675	0.626
2f1	2400	0.250	107	44.72	2.88	86.94	17	24.8	31.0	45.9	43.2	0.37	0.39	0.878	0.778
2f2	2700	0.250	120	44.72	3.24	86.86	17	25.8	32.9	48.7	45.8	0.35	0.37	0.878	0.777
2f3	2700	0.239	120	44.72	3.24	61.38	23	25.4	32.9	48.7	38.5	0.47	0.60	0.878	0.549
2f4	7500	0.51	334	44.72	9.0	115.97	26	46.0	54.8	81.2	88.2	0.32	0.29	0.879	1.037
2f5	11000	0.463	489	44.72	13.18	83.19	33	50.6	66.3	98.3	90.4	0.34	0.37	0.878	0.743
2f6	11400	0.510	507	44.72	13.67	81.63	37	52.9	67.5	100.1	91.2	0.37	0.41	0.879	0.730
2f7	12500	0.583	557	44.72	15.0	75.21	46	57.0	70.7	104.8	91.7	0.44	0.50	0.879	0.673

[a] sin $(\theta/2)$ is 0.86 for polymers 1a, 1b, 1c, and 2c, 0.83 for 2d, 2e, and 2f, 0.84 for 2b, and 0.845 for 2a. All radii of gyration, R_H, l_0, A, and L_w values are in angstrom units. A was calculated from L and R_{Gfd}.

It should be noted, however, and this might be a case in point, that relatively low molecular weight polymers do occasionally show an a value far smaller than the a values exhibited by the corresponding high molecular weight homologues.[39,40]

Hydrodynamic radii, R_H, were calculated from diffusion measurements by photon correlation spectroscopy (PCS)

$$R_H = kT/6\pi\eta_s D \qquad (9)$$

where D is the diffusion coefficient (cm^2/s), η_s is the solvent viscosity, and k and T retain their usual meaning. In the case of the 2f family, the relationship

$$D = 3.60 \times 10^{-5} M_w^{-0.533} \qquad r = -0.964$$

was found to hold.

A comparison of the R_{Gfd} values (eq 7) with R_G's calculated according to other models, in Table I, indicates that among the poly(ester amides) there exists a reasonably good agreement between R_{Gfd} and R_{Gfr}. This agreement lends support to our belief that the poly(ester amides) behave as fully or highly draining coils whose dimensions fall within the range of expectation for freely rotating joints connecting long rodlike segments.

The reasonably good agreement between R_{Gfd} and R_{Gfr} for the poly(ester amides) indicates, we believe, that the R_H values used for the determination of R_{Gfd} and calculated from the PCS-measured diffusion coefficients are correct. Thus, one can obtain valid R_H values by PCS even for polymers with small N and rather large l_0.

The R_{Gfd} values of the polyamides are substantially larger than the corresponding R_{Gfr} values. A division of the R_{Gfd} values by $3.3^{1/2}$ (eq 8) produces R_{Gnd}, which turned out to be 79.9, 69.8, and 78.1 Å for polymers 1a, 1b, and 1c, respectively. These values are very close to R_{Gvisc} for the same polymers, indicating that the three polyamides behave as nondraining coils. A fully or highly nondraining behavior is expected from the zigzag polyamides in light of the number of amide groups per unit chain length being twice as large as in the case of the poly(ester amides) and the well-known[41] strong interaction between the DMAc/LiCl solvent system and the polymeric amide groups.

It is of interest to note that the values of A in Table I, obtained from R_{Gfd}, are reasonably close to $A = 3l_0$ for the poly(ester amides). This is in excellent agreement with the relationship $A = 3l_0$ determined by Tanford[34] for the case of freely draining coils. The values of A for the polyamides are substantially larger than $3l_0$. This, again, reflects the free-draining nature of the poly(ester amides) as compared with the highly nondraining nature of the polyamides.

The ratios of R_H to the various radii of gyration are instructive. As is obvious from Table I, the values of R_{Gg} are in many instances very close to those of R_H. Also, many R_{Gvisc} values of poly(ester amides) are similar to the corresponding R_H's. Ratios R_H/R_G in the close neighborhood of unity are not acceptable,[34] and the indication is that the calculated R_{Gg} and R_{Gvisc} are substantially smaller than the true R_G. The ratios R_H/R_{Gfr} and R_H/R_{Gfd} are listed in Table I. It is tempting to claim the ratios to be inversely dependent on M_w (as in the 2a family) as well as on l_0 (among the polyamides and from comparison of the average ratio for family 2a with the average ratio for family 2f), but the data are too scattered to draw firm conclusions. The decrease in values of R_H/R_{Gfr} with increased chain length, among the four 2a homologues, is in agreement with theoretical predictions for chains of relatively small N values.[42] The decrease in R_H/R_{Gfr} and R_H/R_{Gfd} with increasing l_0 length is observed when the averaged ratios of the poly(ester amide) families are compared and among the three polyamides. This is expected since an increase in l_0 renders the coil more open and better draining. The R_H/R_{Gfr} ratios for the large majority of our zigzag polymers are substantially smaller than 0.54. This last value was calculated[43,44] to be the smallest possible value for the fully swollen, freely jointed Gaussian chain model. The small R_H/R_{Gfr} and R_H/R_{Gfd} ratios indicate that the zigzag polymers are not conventional Gaussian coils but are more expanded, freely rotating coils. It should be noted that the R_H/R_{Gfr} values for the zigzag polymers appear to fall around the values recently determined by Bishop et al.[45] for poly(aryl ether ketone) (PEEK), which can be visualized as a zigzag polymer with virtual bonds 5.56 ± 0.06 Å long.

Values of R_{Gw} calculated according to eq 3 from the known L and with the assumption that $A = 3l_0$ are presented in Table II. The ratios R_H/R_{Gw} fall in the range expected for well-draining coils. The ratios R_{Gw}/R_{Gfd} and R_{Gw}/R_{Gfr}, being generally in the vicinity of 1.0, indicate the

Table II
Light Scattering Results of Poly(ester amides)[a]

polymer	M_w	N	R_H	dn/dc, mL/g	R_{Gw}	R_H/R_{Gw}	R_{Gw}/R_{Gfd}	R_{Gw}/R_{Gfr}
2a4	16 700	49	43	0.248	88.0	0.49	0.96	1.04
2c	32 200	55	64	0.150	157.8	0.41	1.02	0.96
2f1	2 400	2.88	17	0.212	31.4	0.54	0.73	0.68
2f2	2 700	3.24	17	0.221	34.7	0.49	0.76	0.71
2f3	2 700	3.24	23	0.209	34.7	0.66	0.90	0.71
2f4	7 500	9.00	26	0.217	75.7	0.34	0.86	0.93
2f5	11 000	13.18	33	0.219	97.8	0.34	1.08	0.99
2f6	11 400	13.67	37	0.219	100.2	0.37	1.10	1.00
2f7	12 500	15.00	46	0.210	106.2	0.43	1.16	1.01

[a] All distances are in angstrom units.

Table III
Characteristic Molecular Weights for Entanglement

polymer	M_w	M_0	d, g/cm^3	C_c, vol/vol %	C_cM_w	C_cM_w/M_0
			Polyamides			
1a	24 000	211	1.357	2.03	490	2.51
1b	18 000	330	1.359	2.66	480	1.45
1c	22 000	449	1.371	2.40	530	1.18
			Poly(ester amides)			
2a4	16 700	343	1.273	2.68	450	1.35
2b	6 100	339	1.31	6.25	380	1.12
2c	32 200	584	1.353	1.48	480	0.82
2d	16 000	641	1.309	2.44	390	0.61
2e1	10 000	646	1.315	2.36	240	0.37
2f7	12 500	834	1.305	3.61	430	0.52

free-draining freely rotating coil to be the best model describing the dilute solution behavior of the zigzag poly(ester amides).

Transition Regime. The viscosities of all zigzag polymers were determined on solutions of up to 15 wt/vol % concentration. Using the polymer density values in Table III, the concentrations were converted to vol/vol %, and log–log plots of η_0 against vol/vol concentration, C, were prepared for all the zigzag polymers in this study. All plots indicated that for polymers with $M_w \gtrsim 10\,000$ the linear part of the high-concentration branch of the curve had slopes in the range 3.33–4.26. This high power dependence of the solution viscosity η_0 on concentration indicates that at concentrations of 10–15% the higher M polymers are in the concentrated solution regime and that the level of chain interpenetration and entanglement is high.[46] For these polymers, the steepness of the slope appears to increase with increases in either M_w or l_0. The polymers with $M_w < 7000$ failed to show such high power dependence in the $10\% \leq C \leq 15\%$ interval, indicating they did not reach the high-concentration regime. At this concentration interval their power dependence was in the range 2.00–2.50. The above indicates that M_c, the critical molecular weight for entanglement, is at least 1000 for all polymer families in this study and is approximately constant.

From the characteristic concentration C_c, defined as the point of intersection of the linear extrapolation of the two branches describing the dependence of log η_0 on log C, one obtains C_cM_w, a characteristic molecular weight. Values of C_c and C_cM_w for several polymers are presented in Table III together with the values of M_0, the molecular weight of segments with virtual bond length l_0, and the ratio C_cM_w/M_0. A comparison of the C_cM_w values with M_c indicates that the C_cM_w values are between half and one-quarter the relatively constant M_c values. By analogy with several "engineering thermoplastics",[6,7,12] we believe that the value of $M_c \geqslant 1000$ is reasonable.

Within each of the zigzag polymer families, the ratios C_cM_w/M_0 and M_c/M_0 decrease with increased l_0, while C_cM_w remains constant. The constancy of C_cM_w and the approximate constancy of M_c mentioned above indicate that for the zigzag polymers the onset of entangled behavior depends on the concentration of virtual bonds and not on the length of individual rodlike segments.

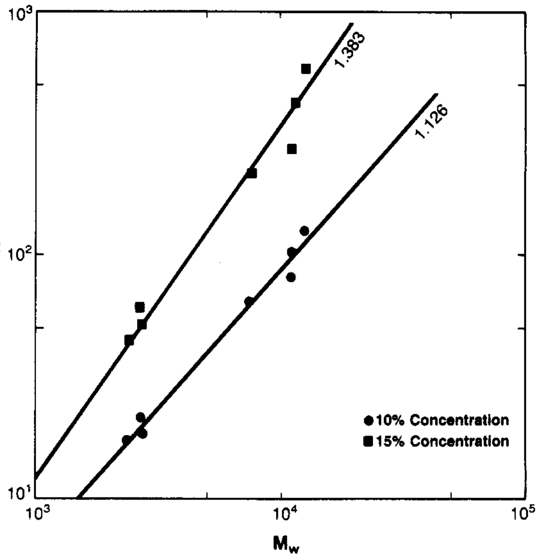


Figure 1. Zero-shear viscosity as function of M_w of the 2f series at high concentrations. All in DMAc/5% LiCl at 25 °C.

Finally, it should be noted that in all instances the measured solvent viscosity, η_s, was between 2.34 and 2.42 cP. The zero-shear viscosities at 1% never fell below 4.0 cP and rapidly increased with concentration. This means that in the transition regime η_0/η_s never fell below 1.65, making possible solvent effects on C_c negligible.

Concentrated Solution Regime. We have noted above that for polymers with $M_w \gtrsim 10\,000$ there exists in the concentration interval of 10–15% a power dependence of the zero-shear viscosity on concentration ranging from 3.33 to 4.26. In addition to the concentration dependence, a dependence of η_0 on the molecular weight M_w and on the rodlike segment length l_0 was also observed. In Figure 1 the zero-shear viscosity of the seven members of the 2f family, reaching to only $M_w \leqslant 12\,500$, is plotted on log–log paper against M_w. The straight lines follow the dependencies at 10% concentration, $\eta_0 = 2.684 \times 10^{-3} M_w^{1.126}$ ($r = 0.9937$) and at 15% concentration, $\eta_0 = 9.826 \times 10^{-4} M_w^{1.383}$ ($r = 0.9858$). These relationships indicate that in the 10% concentration most, if not all, members of the 2f family are still in the nonentangled region and that entanglement effects just start to become noticeable at 15% concentration. In light of this, one can draw only qualitative and tentative conclusions from the viscosity results at 15% concentration, presented in Table IV. The viscosities at 10% concentration are presented in this table for the purpose of comparison with other polymers.

Table IV
High-Concentration-Solution Viscosity[a]

polymer	M_w	η_0 at 10%	η_0 at 15%	η_c/L_w	100 × η_0/M_w
		Polyamides			
1a	24 000	432.2	1745.0	1.551	7.271
1b	18 000	238.5	1390.0	1.716	7.722
1c	22 000	313.0	1945.0	1.945	8.841
		Poly(ester amides)			
2a4	16 700	74.6	252.9	0.328	1.514
2c	32 200	195.1	747.4	0.505	2.321
2d	16 000	85.5	316.6	0.480	1.979
2e1	10 000	96.4	405.7	0.922	4.057
2f1	2 400	17.2	44.9	0.420	1.871
2f2	2 700	21.2	60.7	0.505	2.248
2f3	2 700	18.4	52.3	0.435	1.937
2f4	7 500	63.6	219.7	0.658	2.929
2f5	11 000	81.0	272.7	0.557	2.479
2f6	11 400	100.0	428.9	0.845	3.762
2f7	12 500	126.4	582.7	1.046	4.662

[a] All viscosities are zero-shear viscosities in centipoises. Solvent (DMAc/5% LiCl) viscosity about 2.4 cP. All measurements at 23 °C.

In the last two columns in Table IV are listed the values of η_0 normalized with respect to L_w, the projected chain length, and with respect to M_w, respectively. Analysis of the η_0/L_w and η_0/M_w data of the three polyamides and of the highest M poly(ester amides) 2a4, 2c, 2d, 2e1, and 2f7, indicated a weak dependence of these normalized viscosity values on the length l_0 of the corresponding zigzag polymers. No quantitative conclusions could be drawn from the available data. A qualitative study of 35% solutions in DMAc/5% LiCl of polymers 2a3 and 2f7, of essentially the same molecular weight, indicated that, after being kept for 6 mo at room temperature, the solution of poly(ester amide) 2a3 flows far faster than the solution of the 2f7 poly(ester amide). This leads us to believe that the viscosity dependence on l_0 will become more pronounced with increased concentration. At present, however, we have no additional data to support this assertion.

The viscosities of 10 and, naturally, 15 wt/vol % solutions of all our zigzag polymers in DMAc/5% LiCl are far higher than the viscosities of common flexible polymers of comparable and somewhat higher molecular weights. For example, a 20 wt/vol % solution of polystyrene of $M_v = 30\,000$ exhibited $\eta_0 = 10$ cS,[47] and an 11 wt/vol % solution of poly(ϵ-caprolactam) of $M_w = 42\,650$ in formic acid has a viscosity of 70 cS.[48] (The density of DMAc/5% LiCl is very close to 1.00 g/cm^3, making viscosities in centistokes comparable to viscosities in centipoises.) It should be noted that the higher viscosity of the poly(ϵ-caprolactam) is in large measure due to strong hydrogen-bond-type interactions with the acid, causing a substantial coil expansion in it.[49] However, even with these strong interactions and coil expansion, the viscosity of the poly(ϵ-caprolactam) was smaller than that of all the zigzag polymers with about half its molecular weight. The higher viscosities reflect, we believe, the expanded coil state of the zigzag polymers in the concentrated solution regime and the high level of coil interpenetration and chain entanglement. The much higher viscosities of the zigzag polyamides might reflect the larger number of hydrogen-bond-type interactions between polymer and solvent possible in the case of these polymers as compared with zigzag poly(ester amides) of comparable molecular weight.

Highly concentrated solutions were prepared from all zigzag polymers in this study. The solvents of choice were hot or cold DMAc/5% LiCl and cold concentrated sulfuric acid. All true solutions in concentrations up to and including 35 wt/wt % polymer were found to be isotropic in the quiescent state. Such solutions were fully transparent and fluid, with honey consistency, and retained their initial appearance after at least 3 mo at ambient temperature. This indicates these solutions not to be transparent gels and that no optical-scale phase separation existed in them or formed with time. At higher than 35% concentration, swollen polymeric gels appeared in amounts that increased with total polymer concentration. No stir opalescence could be induced in any of the gel-free solutions. Unless stress was applied to the gel particles, no birefringence was observed in them. This behavior of the zigzag polymers is unlike that of the rodlike poly(ester amide), which exhibited lyotropic liquid crystallinity at concentrations of 30% and above and was as well a thermotropic liquid crystal.

Bulk Polymers. Combined results of DSC, TGA, and cross-polarized light hot-stage microscopy showed no thermotropic liquid crystallinity by any of the zigzag polymers up to the onset of their thermal degradation. In the case of the polyamides this occurred at 480 °C and above. The degradation of the poly(ester amides) started at about 420 °C, and no first-order transition was observed at lower temperatures. In the case of polymers 2e and 2d relatively sharp peaks giving the appearance of a possible first-order transition were observed in the DSC scans at 385 and 365 °C, respectively. However, microscopy observations revealed that rapid discoloration started at these temperatures, which was not attended by transition to liquid crystalline or isotropic melt phases. It should be concluded, then, that the zigzag polymers in this study fail to show lyotropic as well as thermotropic liquid crystallinity.

The failure of our zigzag polymers to exhibit mesomorphicity stands in contradistinction to theoretical expectations in the literature.[1,50–54] The theoretical treatments modeled the macromolecules each as a sequence of rodlike segments connected to one another by flexible spacers, making the spatial orientation of each rodlike segment essentially independent of the orientation of its adjacent rods. In our case the situation is fundamentally different. The spatial orientation of each rodlike segment is limited to a cone defined by the free rotation of one segment at a fixed angle relative to its neighboring rodlike segments.

Wide-angle X-ray diffractometry of the zigzag polymers revealed all the poly(ester amides) to be amorphous and the polyamides to be substantially crystalline with a crystallinity index of 47 ± 3%.

The densities of the zigzag polymers were determined by pycnometry in order to determine whether the length l_0 of the rodlike segments and the constant angle of their cone of rotation hinder close packing of the polymers in the solid state. They are all listed in Table III. In addition to specimens comprising one zigzag polymer each, specimens were prepared from a mixture of poly(ester amides) 2a and 2e obtained by precipitation in excess methanol from a single isotropic 20% solution containing 10 wt/vol % of each polymer. The density of the amorphous mixture was measured to be 1.288 g/cm^3. Comparison of our results with literature densities of amorphous and semicrystalline polyamides,[55,56] polyesters,[57–60] and a group of low molecular weight poly(ester amides)[9] indicates that the densities of our zigzag polymers are within the range of expectation for amorphous poly(ester amides) and partly crystalline polyamides. Therefore, we conclude that the nature of the zigzag polymers does not prevent them from packing densely in the solid bulk and that no excessive free volume is present in the system. This conclusion is valid also for the mixture of the two poly(ester amides) described above.

Conclusions

To summarize our observations: In dilute solutions at $C \ll C_c$, the behavior of the zigzag polymers is dictated by their freely rotating joints, with their rodlike segments acting as long virtual bonds in freely rotating random coils. The poly(ester amides) behave as highly draining coils, while the polyamides are nondraining. The size of the zigzag polymer coils is clearly dependent on l_0. Their Kuhn segment length equals three virtual bonds: $A = 3l_0$. In concentrated solutions, at $C \gg C_c$, the solution behavior is dominated by M_w and C, and, to a lesser extent, by l_0. The effect of virtual bond length is especially noticeable when the viscosity is normalized to remove the effects of differences in chain length. At very high concentrations the zigzag polymers do not form lyotropic liquid crystals despite the fact that their rodlike segments are of sufficient length to form anisotropic solutions. In the bulk, the zigzag polymers do not form thermotropic liquid crystals. A chemically similar rodlike poly(ester amide) forms both lyotropic and thermotropic liquid crystals. The density of the semicrystalline zigzag polyamides and, especially, the amorphous zigzag poly(ester amides) indicates that the polymeric chains are closely packed together with no apparent hinderance due to the length of the rodlike segments and the fixed angle defining their cones of free rotation.

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Registry No. **1a** (copolymer), 28853-54-5; **1a** (SRU), 26854-94-4; **1b** (copolymer), 28853-50-1; **1b** (SRU), 31868-46-9; **1c** (copolymer), 106822-00-8; **2a** (SRU), 106821-96-9; **2a** (copolymer), 106822-01-9; **2b** (SRU), 106821-97-0; **2b** (copolymer), 106822-02-0; **2c** (copolymer), 106822-03-1; **2c** (SRU), 106835-86-3; **2d** (copolymer), 106822-04-2; **2d** (SRU), 106835-87-4; **2e** (copolymer), 106822-05-3; **2e** (SRU), 106821-98-1; **2f** (copolymer), 106822-06-4; **2f** (SRU), 106821-99-2; A, 106821-92-5; B, 32001-91-5; C, 17074-58-7; D, 106821-94-7; E, 106821-93-6; F, 106821-95-8.

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