negative charge stability on less substituted carbon atoms. In allyllithium[16] the two positions are equivalent, but in crotyllithium[17,18] substitution makes the γ position less favored for charge. Nevertheless, the increased charge at the γ position leads to high 1,2 contents in the polymer formed.

It is possible to suppose, as have other authors,[13] that a delocalized structure exists only in THF and that the benzene-stable form of the active center is a separate covalent form. The spectral shifts observed in THF mixtures would result as long as equilibration was rapid on the nmr time scale. It seems to us more plausible to regard the changes as caused by variable charge delocalization as the local environment is changed. Even in benzene solution there is evidence for some charge at the γ position, and the appearance in both hydrocarbon and ether solvents of similar ultraviolet absorption bands[19] argues against a covalent form in the former solvents. The evidence in diethyl ether solutions at -70° for a weak γ absorption at about the same position as in benzene, as well as the expected stronger upfield absorption,[13] could have other explanations than slow equilibration between covalent and ionic forms. Apart from the danger inherent in analysis of very weak signals in such systems, the presence of residual amounts of aggregated structures not completely destroyed by ether can be suggested, *i.e.*, slow equilibration between associated and dissociated forms under these conditions. This is evidently not the case with the stronger base THF, for even at -80° no extra γ signals are observed. In addition, the γ absorption still drifts upfield after more THF has been added than is required to dissociate the aggregates.

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Degree of Association of Polystyryl-, Polyisoprenyl-, and Polybutadienyllithium in Hydrocarbon Solvents

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ABSTRACT: The degrees of association of living polymers of styrene, butadiene, and isoprene (Li counterion) have been evaluated principally by means of light-scattering measurements in cyclohexane. Some determinations were made using concentrated solution viscosities. It was confirmed that the association number was two for the styrene compound and four for the butadiene and isoprene polymers. The latter polymer shows partial dissociation to dimers at low concentrations. The difficulties encountered in interpretation of concentrated solution viscosity measurements in these systems are described. It is suggested that these difficulties are responsible for the discordant values of association number found in the literature.

The active chain ends of polymers formed by the action of lithium alkyls on hydrocarbon monomers are associated in hydrocarbon solution.[1–6] There has, however, been disagreement concerning the degree of association. Some reports suggest that it is twofold in all cases,[6] but others state that it varies with the monomer involved.[7–10] Similar disagreements existed in the past about the kinetic order of the propagation reaction in these polymerizations. A half-order with respect to the active chain ends in all cases[11] has been suggested, but other studies found that the order varied with the monomer involved.[2–5,7–9] By the application of improved techniques these differences have been resolved and, it is more generally accepted that the order varies with the monomer.[12]

Unfortunately, whereas in the past there was general agreement that association number and kinetic order were connected, at present there exists, in some reports, a discrepancy.[6,12] Until this is resolved the proposed mechanism of the reaction must be in doubt, as the only detailed mechanism suggested[1] involves the monomeric dissociation product of the aggregates as active species in polymerization. This requires, for a labile equilibrium, that the kinetic order be $1/n$ if the association number is n.

The generally accepted orders for the propagation reaction in the polymerization of styrene, isoprene, and butadiene initiated by lithium alkyls in hydrocarbon solvents are one-half for styrene and one-quarter or less for the dienes. There is general agreement that the degree of association for polystyryllithium is two. A previous report from these laboratories suggested that for polyisoprenyllithium the degree of association was between three and four and that equilibrium might exist between dimer and tetramer leading to a kinetic order close to one-fourth for the reaction.[10] This work has been repeated over a wider range of concentrations and ex-

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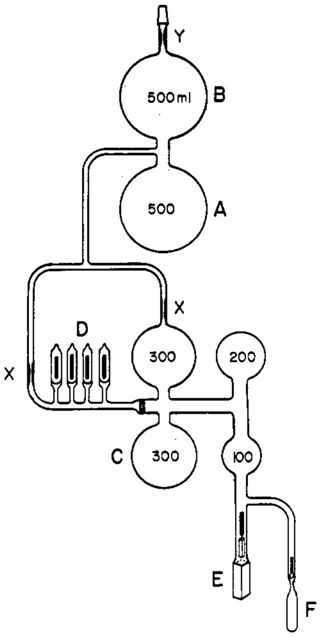

Figure 1. Apparatus for light scattering on living polymers: (E) optical cell for concentration measurements, (F) light-scattering cell to fit Sofica instrument. Other letters refer to text.

tended to butadiene to see if the earlier report could be confirmed. The method used was light scattering on living polymers under θ conditions. To supplement these measurements some concentrated solution viscosities were also measured on polystyryllithium before and after capping with isoprene.

Experimental Section

The purifications of the solvents and monomers have been described before.[7-9] The initiator used was 2-butyllithium to ensure that the molecular weight distribution was narrow. This was initially distilled by a short-path distillation into a break-sealed vessel and later distilled from there into the reaction vessel.

The concentrations of the polystyrene and of the active chain ends in the light-scattering experiments were determined *via* their uv absorption by means of a quartz optical cell attached to the reaction vessel. The cell had a 0.9-cm quartz insert which could be moved in and out by an attached glass-covered magnet.

The light-scattering measurements were made in a cylindrical cell of selected glass attached to the reaction vessel. The cell had a metal collar designed to fit a Sofica light-scattering instrument. It could be closed off by a magnetically operated seal to isolate the cell held at 35° from upper, cooler parts of the apparatus. A schematic diagram is shown in Figure 1. The actual construction was not planar, but curved, so that it would balance when inserted in the light-scattering instrument. It was of such a size that it would fit a light-tight box built onto a Cary-14 spectrophotometer. The vessel (A) was evacuated and half-filled with a dilute solution of butyllithium in cyclohexane. After removal from the vacuum line at Y, the walls of the vessel were purged with catalyst. Inversion of the apparatus enabled the walls to be rinsed with solvent by refluxing solvent from B. The solvent was then distilled into C by appropriate manipulation and the section A, B was sealed off and removed at X. The breakseals (D) contained the initiator, the styrene, the diene, and methanol.

The 2-butyllithium and then the styrene were distilled into solvent in one of the remaining flasks after the breakseals were broken. After the formation of and measurements on polystyryllithium, the diene was added, and last of all the methanol. At each stage the concentration of polymer in the cell could be varied by solvent distillation. The optical density at 328 mμ was used to monitor the polystyryllithium concentration to ensure that no destruction of chain ends occurred. The absorbance of the dienyllithium was used to ensure that no termination occurred when the diene was added. The concentration of polystyrene was measured using its sharp absorption maximum at 269 mμ. The initial polymer solution was 6% to ensure as monodisperse a polymer as possible and also to increase the quantity of butyllithium handled.

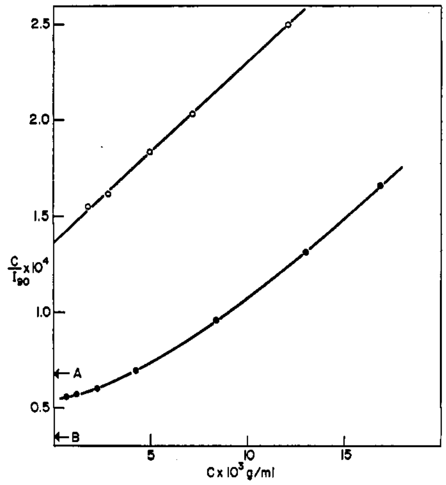

Figure 2. Light-scattering results on polyisoprenyllithium (●) and its terminated polymer (○) in cyclohexane. Base molecular weight 18,000. Arrows at A and B correspond to molecular weights of 36,000 and 72,000, respectively.

Concentrated solution viscosities were measured in a vacuum viscometer at 35°. The vacuum viscometer was purged using techniques similar to those described above. The reagents passed through a filter into the reaction vessel before reaction. Sublimed *tert*-butyllithium was the initiator in this case. The same procedure of first forming polystyryllithium, capping it with isoprene, and killing it with methanol was used. The dimensions of the three viscometers used were similar, all designed to be totally immersed in the thermostat bath. The shear rates were well within the range of laminar flow. They were calibrated against Cannon-Ubbelohde standard viscometers.

Results

An attempt was first made to make light-scattering measurements in cyclohexane solution on polyisoprenyllithium itself. The molecular weights were low (18,000–50,000), so dissymmetry was negligible and only 90° values are shown. The results for the sample of lowest molecular weight are plotted in Figure 2, and show that although the concentration dependence for the dead polymer is normal, that of the living polymer is strongly curved. The more concentrated solution points would suggest an extrapolation to a value indicating a molecular weight several times that of the dead polymer. The more dilute points would give a lower value, but still more than twice the value for the dead polymer. This suggests that the apparent molecular weight varies with the concentration. The system is evidently not satisfactory, as it is not possible to obtain the molecular weight at different concentrations without making assumptions about the virial coefficients of mixtures.

Recourse was then made to a system where the virial coefficient may reasonably be taken as zero. There is no solvent that is both a Θ solvent for polyisoprene or polybutadiene and suitable for anionic polymerization. However, cyclohexane is a Θ solvent for polystyrene, and the association of polystyryllithium is readily measured in it. If a little isoprene is then added to the polystyryllithium, the active chain end is converted to polyisoprenyllithium. The degree

TABLE I
MOLECULAR WEIGHTS OF TERMINATED POLYMERS AND CORRESPONDING POLYSTYRYLLITHIUM

	Killed polymer		Polystyryllithium
Polymer	Mol wt(LS)[a]	Mol wt(OSM)[a]	Mol wt(LS)[a]
A	160,000		347,000
B		24,700	49,800
C		11,100	22,000
D	154,000	153,000	322,000
E		21,800	42,300

[a] LS = light-scattering data; OSM = osmometry data.

TABLE II
APPARENT MOLECULAR WEIGHTS OF POLYSTYRENE CAPPED WITH BUTADIENYLITHIUM IN CYCLOHEXANE AT 35°

Base polymer	$c \times 10^6$, M	Mol wt(app) $\times 10^{-3}$	Degree of association[a]
D	4.18	604	3.95
D	7.25	616	4.03
D	23.07	601	3.93
D	37.7	591	3.86
D	43.6	632	4.13
E	57.3	88.6	4.06
D	65.4	612	4.00
E	109.6	91.9	4.22
E	183.9	91.7	4.21
E	232.1	93.7	4.30
E	355.5	92.6	4.25
E	500	93.5	4.29
E	718	93.3	4.28
E	762	94.1	4.32

[a] Number averages, converted from the weight averages actually observed on the assumption that the base polymers are monodisperse.

TABLE III
APPARENT MOLECULAR WEIGHTS OF POLYSTYRENE CAPPED WITH ISOPRENYLLITHIUM IN CYCLOHEXANE AT 35°

Base polymer	$c \times 10^6$, M	Mol wt-(app)[a] $\times 10^{-3}$	Degree of association
A	4.89	445	2.78
A	11.8	448	2.80
B	16.1	77.9	3.12
B	27.1	82.6	3.30
A	30.0	534	3.34
B	38.0	85.1	3.40
A	40.9	538	3.37
A	59.2	541	3.38
B	65.5	87.6	3.50
B	127.5	94.8	3.79
C	194	43.2	3.91
B	223	100.8	4.03
B	307	102.7	4.11
C	376	44.2	4.00
B	439	103.8	4.15
C	472	44.5	4.02
C	676	45.3	4.10
C	804	45.6	4.12

[a] app = apparent.

TABLE IV
CONCENTRATED SOLUTION VISCOSITIES OF ACTIVE AND TERMINATED POLYMERS (28.2% (w/w) at 35°)

			Viscosity, P		
Base polymer	$10^3\overline{M}_n$	Solvent	Base polymer	Polystyryllithium	Isoprene capped
Polystyrene 1	82.6	c-Hexane	1.43	6.06	11.7
Polystyrene 2	217	c-Hexane	15.4	76.1	149
Polystyrene 3	253	c-Hexane	27.0	148	270
Polystyrene 4	385	c-Hexane	72.6	671.4	894.4
Polyisoprene 1[a]	112	c-Hexane	14.4		218

[a] This sample was a pure polyisoprene, not an isoprene-capped polystyrene. The concentration in this case 27% (w/w).

of association will be characteristic of polyisoprenyllithium, but the bulk of the polymer is still polystyrene and will still have zero virial coefficient in this Θ solvent. Hence, molecular weights may be measured at different concentrations of active chain ends.

Such light-scattering measurements were made on several polymers. Table I lists the molecular weights of the dead polymers and the polystyryllithium precursors. The molecular dimensions in the Θ solvent in most cases were sufficiently low that Zimm plots were not necessary. However, some anomalous scattering at low angles was observed, presumably caused by fine glass particles from the breakseals. But, as the ratio C/I_Θ was essentially constant from 150° to 75° for molecular weights less than 200,000, only these values were used in the extrapolation to zero angle when the molecular weights were above this figure. As expected, the virial coefficient was zero within experimental error.

Table II lists the concentrations of polystyrenes capped with the butadienyllithium, the molecular weight calculated from the scattering assuming a zero second virial coefficient, and the apparent degree of association. The higher molecular weight series has a molecular weight near 600,000, but as it is a star-shaped polymer its radius of gyration is much smaller than for the comparable linear polymer. Hence the angular dependence of the scattering was quite low in a Θ solvent, and the extrapolation method above was used. From these extrapolations the dissymmetries (45°/135°) were 1.07–1.08, and the actual measured ones were 1.09–1.10 because of the anomalous scattering mentioned above. The degree of association of the living ends appears to be near fourfold over a wide concentration range.

Table III contains the equivalent data for the polystyrenes capped with isoprenyllithium. The variation of molecular weight with concentration is clearly illustrated.

The concentrated solution viscosities are shown in Table IV. It is apparent from the viscosities that there is an increase when the polystyryllithium is capped with isoprene to give the isoprenyllithium chain end and an even greater drop when the polymer is killed.

Figure 3 is a logarithmic plot of the viscosities in cyclohexane solution of the polystyrene polymers, living, dead, and capped, against molecular weight. The molecular weights of the polystyryllithium and isoprenyllithium capped polymers were taken as twice and four times the molecular weight of the dead polymers. The concentration of living ends was in the region where the polyisoprenyllithium appeared close to tetrameric in the light-scattering experiments. The dead polystyrenes and the polystyryllithiums fall on one line as they are all linear polymers. For comparison, the results of Graessley, *et al.*,[13] on linear polystyrenes in *n*-butylbenzene

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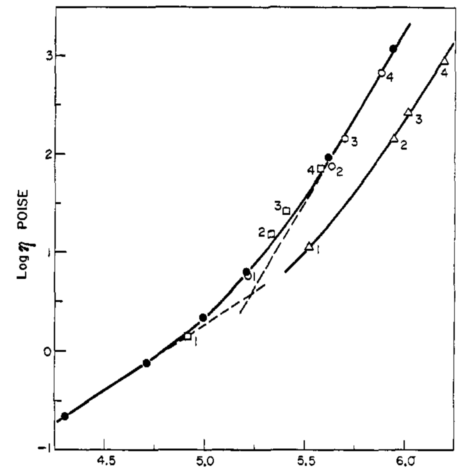

Figure 3. Concentrated solution viscosities in cyclohexane at 35° of terminated polystyrene (□), corresponding polystyryllithium (O), and isoprenyllithium-capped polystyrene (△). The numbers refer to the polymers described in Table IV. (●) Results of Graessley, *et al.*, (28% w/w) in butylbenzene at 30°.

are included. The isoprene-capped polymers fall on a lower line as expected for four-star polymers.

Discussion

It is evident from the light-scattering molecular weight data on the polystyrenes, polystyryllithiums, and polystyrenes capped with isoprenyllithium or butadienyllithium that polystyryllithium is twofold associated, polybutadienyllithium is fourfold associated, and that the association of the polyisoprenyllithium varies with the concentration of living ends.

The highest concentration of butadienyllithium appears to have a molecular weight that has drifted above that expected of a fourfold associate. This 7 or 8% variation is close to the experimental error, but the possibility of higher aggregates at higher concentrations exists. Nevertheless, even to a very low concentration the living ends remain tetrameric.

The degree of association found for polyisoprenyllithium varies over a range greater than could be accounted for by the experimental errors. The highest concentration of active chain ends seems to level out at a fourfold association, but at the lowest concentrations covered this has dropped to below a threefold average. This is interpreted as a dissociation of a tetramer into a dimer with dilution. The dissociation constant calculated is 6×10^{-6}. Appreciable dissociation into a monomeric form is not likely, and is confirmed by the fact that a constant dissociation constant cannot be obtained if this possibility is considered.

With the concentrated solution viscosity technique, the region in which η is proportional to $M^{3.4}$ is used with the aim of increasing the accuracy of the determinations. This law only holds above a critical molecular weight which depends on the polymer and its concentration. Figure 3 illustrates the difficulties which can occur with polystyrene. Porter and Johnson[14] have evaluated a large amount of published data and suggest that the best value of $(Nv)_c$ in this case is 857[15] (N = the number of backbone carbon atoms, v is the volume fraction of polymer, and subscript c refers to the breakpoint between the ~1.5 and 3.4 power laws in N). With our experimental conditions M_c would be ~200,000. There is, however, no sharp breakpoint and molecular weights appreciably above 200,000 are required before the 3.4 law is fully effective. This is confirmed by the results of Graessley, *et al.*,[13] shown in Figure 3. The close agreement of the absolute viscosities of these authors with those determined in this work is perhaps fortuitous, because slightly different temperatures and a different solvent were used. The curvature is nevertheless apparent. Because the polystyrenes used span the range above and below M = 200,000, the ratio of viscosities of living and dead polymers increases with the molecular weight and only approaches the expected tenfold ratio ($2^{3.4}$) at the highest molecular weights. There is, however, little doubt that polystyryllithium is twofold associated as judged by the light-scattering results and the fact that the "living" and "dead" samples fall on the expected smooth curve. The method is clearly not as attractive as expected because of the very high value of M_c at reasonable concentrations of polystyrene together with limitations on the concentration and molecular weight of living polymer systems.

The viscosity values for the isoprene-capped polymers fall on a different (lower) line if plotted on the basis of fourfold association as in Figure 3. This is as expected because four-star branched polymers show an appreciably lower viscosity than linear polymers of the same molecular weight. M_c is also increased and the 3.4-power law only holds for $M >$ 500,000 in 28% solutions of polystyrene. In this range of molecular weight the viscosity of a four-star polystyrene is close to 0.12 that of a linear polymer of the same molecular weight in diethylbenzene.[16] This produces the result that the viscosities of a linear molecule of DP = $2N$ and a star molecule of DP = $4N$ are not very different, although the difference should be measureable. This point can also be seen in Figure 3. The points for the isoprene-capped polymers fall close to the expected values for a four-star polymer when plotted assuming an association number of four. If a twofold association had been assumed for the capped polymer, the points would have fallen only slightly above the line for linear polymers. All the expected sensitivity of the method for the determination of association numbers has disappeared because of the drastically reduced viscosities of the branched species. Thus, although there was a definite measurable increase in viscosity on capping with isoprene which suggests fourfold association, the method cannot be recommended as a diagnostic tool.

Another possible failing of the method appears not to have been considered. For all associated living polymer systems the link points are not permanent. In order to achieve near-monodisperse polymers with these systems, it is necessary to postulate a moderately rapid dissociation and reassociation between different species. This could provide an alternative relaxation mechanism and hence lead to lower viscosities. In Figure 3, in fact, the points for polystyryllithium do tend to be slightly low, which might suggest a small contribution from this effect, although clearly it is not of great importance and may in fact be simply experimental error.

The results obtained here do not agree with those reported by Morton and coworkers in the case of butadiene and isoprene. Some comment on these discrepancies is clearly necessary. Most of the evidence presented for twofold association relies on concentrated solution viscosity measurements. These are made at relatively high concentrations of active centers, so association numbers of four even for polyisoprenyllithium should have been obtained. The difficulties

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[16] J. E. L. Roovers and S. Bywater, unpublished results.

of interpretation have been pointed out above, and in fact seem responsible for the differences observed. In general, where this can be checked, the molecular weight of the base polymer appears to have been close to or less than M_c at the particular concentration used. This must lead to low values of viscosity increase on association. For instance, the isoprene-capped polystyrenes[6] were either used at $v = 0.14$, $M = 260{,}000$ or $v = 0.30$, $M = 139{,}000$. M_c is 320,000 or 150,000, respectively, under these conditions. Molecular weights at least 100,000 above M_c are necessary before the 3.4 law becomes accurate for styrene. Similar conditions seem to have been used for polyisoprenyllithium itself in benzene. With polyisoprene the critical molecular weights at a given volume fraction are lower than with polystyrene solutions, and it is easier to attain the region of validity of 3.4 law. Nevertheless, the original data[17] suggest that a volume fraction of 0.16 was used for two polymers of M = 80,000 after killing. The value of M_c at this concentration is 88,000.[18] Two other polymers were used at a volume fraction of 0.26 where M_c will be 54,000; their molecular weights were ~74,000 and ~110,000. These two polymers gave 13-fold and 15-fold changes in viscosity, respectively, between the isoprene-capped and terminated polymers, whereas the first two gave 10-fold increases. Clearly, although the latter two experiments were dismissed as being caused by experimental error, what was really observed was an increase in the viscosity ratio as conditions approached the region of validity of the 3.4-power law. In fact, a 15-fold change of viscosity was observed by us under appropriate experimental conditions (Table IV). This is approximately what would be expected for fourfold association. We cannot be exact about this because we have presently no data on four-star polyisoprenes, but we suppose that the difference in viscosity of four-star polyisoprenes compared to linear polymers is about the same as for polystyrenes.

The light-scattering measurements indicating an association number of two for polyisoprenyllithium were made in *n*-hexane.[6] We have shown that in the similar good solvent for polyisoprene, cyclohexane, extrapolation to zero concentration based on three points is a hazardous procedure, for the line is strongly curved due to partial dissociation (Figure 2). Lower concentrations of active centers are used in light-scattering measurements (down to 10^{-5} M, where the association number is about three). Owing to the changing association number in the concentration range, a meaningful analysis of the results cannot be obtained in a good solvent. Measurements on isoprenyllithium-capped polystyrene in cyclohexane are required to solve this problem.

In summary, we have presented evidence for twofold association of polystyryllithium and fourfold association for polybutadienyl and polyisoprenyllithium. The latter compound dissociates on dilution but does not reach an association number of two at the lowest usable concentrations (~10^{-5} M). The difficulties in using concentrated solution viscosities as a diagnostic tool have been assessed. Without an exact knowledge of the decrease in viscosities of branched polymers compared to linear ones, accurate measurements of association numbers are not obtainable with this technique. The expected accuracy of the method is much lower than expected from simple use of the 3.4-power law. It is difficult to keep in the range of applicability of this law in conventional anionic systems.

Acknowledgment. We are indebted to Dr. J. Prud'homme for the data presented in Figure 2 which was obtained during the tenure of a postdoctoral fellowship at N.R.C.

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Structural Control in the γ-Radiation-Initiated Polymerization of 1-Vinyluracil[1]

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ABSTRACT: Poly(1-vinyluracil) has now been prepared with complete repression of cyclopolymerization *via* γ-radiation-initiated polymerization using the following techniques: (a) polymerization at low temperature, (b) polymerization at high concentrations of monomer, (c) polymerization in the solid state, (d) polymerization of negatively charged monomers, and (e) polymerization of monomers containing bulky substituents. As the temperature was reduced from 0 to −78° the extent of cyclopolymerizations decreased from 20% to 0% in solution. At 0°, high concentrations of negatively charged 1-vinyluracil also led to 0% cyclopolymerization. In the solid state, polymerization occurred at 40° without any cyclopolymerization. At very high doses, some cross-linking was observed. Polymerization of 6-methyl-1-vinyluracil at 25° in solution led to the completely noncyclopolymerized polymer. The polymers were amorphous by X-ray diffraction, and the 100-MHz nmr spectra at 170° in DMSO-d_6 suggested that the poly(1-vinyluracils) varied in their degree of syndiotacticity. The ultraviolet hypochromism at 264 mμ was found to vary widely with the tacticity.

In a previous report from this laboratory it was shown that the free-radical-initiated polymerization of 1-vinyluracil (I) led to a poymer which contained a high percentage of cyclopolymerizated units in the main chain.[4] Although we,[5]

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(2) To whom inquiries should be addressed.

(3) In partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Texas A&M University.

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