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SYNTHESIS AND CHARACTERIZATION OF POLY(ACRYLAMIDE) BY CONTROLLED RADICAL POLYMERIZATION

Rajesh Kumar

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005, UP, INDIA.

ABSTRACT

Successful polymerization of acrylamide was carried out by controlled radical polymerization methodology. The kinetics of controlled radical polymerization was studied and it was found pseudo first order. The conversion was calculated by integration of proton of repeated units.

INTRODUCTION

Polymer chemistry or **macromolecular chemistry** is a multidisciplinary science that deals with the chemical synthesis and chemical properties of polymers or macromolecules. According to IUPAC recommendations, [1][2] macromolecules refer to the individual molecular chains and are the domain of chemistry. Polymers describe the bulk properties of polymer materials and belong to the field of polymer physics as a subfield of physics. Polymer chemistry is that branch of one, which deals with the study of synthesis and properties of macromolecules. Polymers are formed by polymerization of monomers. A polymer is chemically described by its degree of polymerization, molar mass distribution, tacticity, copolymer distribution, the degree of branching, by its end-groups, cross-links, crystallinity and thermal properties such as its glass transition temperature and melting temperature. Polymers in solution have special characteristics with respect to solubility, viscosity and gelation.

Biological synthesis of Polymer:

There are three main classes of biopolymers: polysaccharides, polypeptides, and polynucleotides. In living cells, they may be synthesized by enzyme-mediated processes, such as the formation of DNA catalyzed by DNA polymerase. The synthesis of proteins involves multiple enzyme-mediated processes to transcribe genetic information from the DNA to RNA and subsequently translate that information to synthesize the specified protein from amino acids. The protein may be modified further following translation in order to provide appropriate structure and functioning.

Modification of natural polymers

Many commercially important polymers are synthesized by chemical modification of naturally occurring polymers. Prominent examples include the reaction of nitric acid and cellulose to form nitrocellulose and the formation of vulcanized rubber by heating natural rubber in the presence of sulfur.

Laboratory synthesis of polymers:

Laboratory synthetic methods are generally divided into two categories, step-growth polymerization and chain-growth polymerization [4]. The essential difference between the two is that in chain growth polymerization, monomers are added to the chain one at a time only[5], whereas in step-growth polymerization chains of monomers may combine with one another directly[6]. However, some newer methods such as plasma polymerization do not fit neatly into either category. Synthetic polymerization reactions may be carried out with or without a catalyst. Laboratory synthesis of biopolymers, especially of proteins, is an area of intensive research.

ROUTES OF POLYMERIZATION:

1. **Step-growth polymerization** refers to a type of polymerization mechanism in which bi-functional or multifunctional monomers react to form firstdimers, then trimers, longer oligomers and eventually long chain polymers. Many naturally occurring and some synthetic polymers are produced by step-growth polymerization, e.g. polyesters, polyamides, polyurethanes, etc. Due to the nature of the polymerization mechanism, a high extent of reaction is required to achieve high molecular weight. The easiest way to visualize the mechanism of a step-growth polymerization is a group of people reaching out to hold their hands to form a human chain — each person has two hands (= reactive sites). There also is the possibility to have more than two reactive sites on a monomer: In this case branched polymers are produced.

   Classes of step-growth polymers

   Polyester has high Tg, high Tm, good mechanical properties to about 175°C, good resistance to solvent and chemicals. It can exist as fibers and films. The former is used in garments, felts, tire cord, etc. The latter appears in magnetic recording tape and high grade films.

2. **Chain growth polymerization** is a polymerization technique where unsaturated monomer molecules add on to a growing polymer chain one at a time [7].

   Chain growth polymerization" and **addition polymerization** (also called **polyaddition**) are two different concepts. In fact polyurethane polymerizes with addition polymerization (because its polymerization does not produce any small molecules, called "condensate"), but its reaction mechanism is a step-growth polymerization.

The distinction between "addition polymerization" and "condensation polymerization" was introduced by Wallace Hume Carothers in 1929, and are referred to the type of products, respectively:[2][3]

RECENT TREND IN CHAIN GROWTH POLYMERIZATION

Living polymerization

In polymer chemistry, living polymerization is a form of addition polymerization where the ability of a growing polymer chain to terminate has been removed [1]. This can be accomplished in a variety of ways. Chain termination and chain transfer reactions are absent and the rate of chain initiation is also much larger than the rate of chain propagation. The result is that the polymer chains grow at a more constant rate than seen in traditional chain polymerization and their lengths remain very similar (i.e. they have a very low polydispersity index). Living polymerization is a popular method for synthesizing block copolymers since the polymer can be synthesized in stages, each stage containing a different monomer. Additional advantages are predetermined molar mass and control over end-groups. Living polymerization in the literature is often called "living" polymerization or controlled polymerization. Living polymerization was demonstrated by Michael Szwarc in 1956 in the anionic polymerization of styrene with an alkali metal / naphthalene system in THF. He found that after addition of monomer to the initiator system that the increase in viscosity would eventually cease but that after addition of a new amount of monomer after some time the viscosity would start to increase again [2].

The main living polymerization methods are:

- living cationic polymerization
- living anionic polymerization
- ring opening metathesis polymerization
- group transfer polymerization
- living Ziegler-Natta polymerization
- free radical living polymerization

FREE RADICAL LIVING POLYMERIZATION

Very late in the twentieth century several new methods were discovered which allowed the development of living polymerization using free radical chemistry. These techniques involved catalytic chain transfer polymerization, iniferter mediated polymerization, stable free radical mediated polymerization (SFRP), atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and iodine-transfer polymerization.

- Catalytic chain transfer polymerization
- Iniferter polymerization
- Stable free radical mediated polymerization
- Reversible Addition Fragmentation chain Transfer (RAFT) polymerization
- Iodine-Transfer Polymerization
- Selenium-Centered Radical-Mediated Polymerization
- Telluride-Mediated Polymerization (TERP)
- Stibine-Mediated Polymerization
- Atom transfer radical polymerization

- **Atom transfer radical polymerization** (ATRP) involves the chain initiation of free radical polymerization by a halogenated organic species in the presence of a metal halide. The metal has a number of different oxidation states that allows it to abstract a halide from the organohalide, creating a radical that then starts free radical polymerization. After inititation and propagation, the radical on the chain active chain terminus is reversibly terminated (with the halide) by reacting with the catalyst in its higher oxidation state. Thus, the redox process causes gives rise to equilibrium between dormant (Polymer-Halide) and active (Polymer-radical) chains. The equilibrium is designed to heavily favor the dormant state, which effectively reduces the radical concentration to sufficiently low levels to limit bimolecular coupling. Polymerizations require elevated temperatures (60-120^{o}C).Obstacles associated with this type of reaction is the generally low solubility of the metal halide species, which results in limited availability of the catalyst. This is improved by the addition of a ligand, which significantly improves the solubility of the metal halide and thus the availability of the catalyst but complicates subsequent catalyst removal from the polymer product.

COMPONENTS OF ATRP

There are five important variable components of Atom Transfer Radical Polymerizations. They are the **monomer**, **initiator, catalyst, solvent and temperature**. The following section breaks down the contributions of each component to the overall polymerization.

Monomer

Monomers that are typically used in ATRP are molecules with substituents that can stabilize the propagating radicals; for example, styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile.[5] ATRP are successful at leading to polymers of high number average molecular weight and a narrow polydispersity index when the concentration of the propagating radical balances the rate of radical termination. Yet, the propagating rate is unique to each individual monomer. Therefore, it is important that the other components of the polymerization (initiator, catalysts, ligands and solvents) are optimized in order for the concentration of the dormant species to be greater than the concentration of the propagating radical and yet not too great to slow down or halt the reaction.[6], [7]

Initiator

The number of growing polymer chains is determined by the initiator. The faster the initiation, the fewer terminations and transfers, the more consistent the number of propagating chains leading to narrow molecular weight distributions. [7] Organic halides that are similar in the organic framework as the propagating radical are often chosen as initiators.[6] Alkyl halides such as alkyl bromides are more reactive than alkyl chlorides and both have good molecular weight control.[6], [7]

Catalyst

The catalyst is the most important component of ATRP because it determines the equilibrium constant between the active and dormant species. This equilibrium determines the polymerization rate and an equilibrium constant too small may inhibit or slow the polymerization while an equilibrium constant too large leads to a high distribution of chain lengths. [7]

Selection of Monomer

Poly(acrylamide) (IUPAC **poly(2-propenamide)** or **poly(1-carbamoylethylene)**) is a polymer (-$CH_2CHCONH_2$-) formed from acrylamide subunits that can also be readily cross-linked. acrylamide needs to be handled using best laboratory practice (such as wearing appropriate gloves, lab coat etc. and having safe systems of work) to avoid poisonous exposure since it is a neurotoxin. Poly(acrylamide) is not toxic, but unpolymerized acrylamide can be present in the polymerized acrylamide. Therefore it is recommended to handle it with caution. In the cross-linked form, it is highly water-absorbent, forming a soft gel used in such applications as poly(acrylamide) gel electrophoresis and in manufacturing soft contact lenses. In the straight-chain form, it is also used as a thickener and suspending agent. More recently, it has been used as subdermal filler for aesthetic facial surgery.

Why Chosen Acrylamide for polymerization?

One of the largest uses for poly(acrylamide) is to flocculate or coagulate solids in a liquid. This process applies to wastewater treatment, and processes like paper making. Most poly(acrylamide) is supplied in a liquid form. The liquid is subcategorized as solution and emulsion polymer. Even though these products are often called 'poly(acrylamide)', many are actually copolymers of acrylamide and one or more other chemical species, such as an acrylic acid or a salt thereof. The main consequence of this is to give the 'modified' polymer a particular ionic character.

Another common use of poly(acrylamide) and its derivatives is in subsurface applications such as Enhanced Oil Recovery. High viscosity aqueous solutions can be generated with low concentrations of poly(acrylamide) polymers, and these can be injected to improve the economics of conventional water flooding.

The ionic form of poly(acrylamide) has found an important role in the potable water treatment industry. Trivalent metal salts like ferric chloride and aluminium chloride are bridged by the long polymer chains of poly(acrylamide). This results in significant enhancement of the flocculation rate. This allows water treatment plants to greatly improve the removal of total organic content (TOC) from raw water.

Thus as we have seen that poly(acrylamide) has wide range of application in industries from paper manufacturing and water treatment through oil recovery to soil modification and medical applications. Besides these applications poly(acrylamide) has other multiple applications *viz* as polymer gel dosimeter , for water retention: owing to its high swelling capacity, in electrophoresis for separation of protein and DNA samples, as a model for drug delivery systems: for studying controlled drug release profiles.

Thus, on the basis of these properties of poly(acrylamide), an attempt was made to polymerize acrylamide under controlled and living polymerization condition which makes them more potent and functional and substantially changes the reactivity of the polymers.

EXPERIMENTAL SECTION

Materials and methods

Commercial reagents were used without further purification and all experiments were carried out in N_2 atmosphere. Hydroquinone, 2-bromoisobutyryl bromide, Cu(I)Br, 2, 2'-bipyridyl, acrylamide, and triethyl amine were purchased from Aldrich USA and used as such. All solvents were purchased from Merck Chemicals, India and used further after purification.

Physical measurements

^{1}H NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a JEOL AL 300 FT NMR spectrometer using TMS as an internal reference.

EXPERIMENTAL PROCEDURE

Synthesis of 1,4-bis (2-bromo *isobutyryloxy*) benzene (a bi-functional initiator)

Hydroquinone (0.5412g, 24.6 mmol) and triethylamine (1.38mL, 49.2 mmol) were dissolved in 10 mL of DMF under N_2 atmosphere. 2-bromo-isobutyrylbromide (1.21mL, 49.2 mmol) was added dropwise to the solution at 0ºC. Reaction mixture stirred at room temperature for 24 hr. When reaction was completed, triethyl ammonium bromide was removed by filtration and the solvent was evaporated under vacuum condition. Further, the product was dissolved in 10 mL of ethyl acetate and washed with water followed by an aq.$NaHCO_3$ solution. The organic layer was separated and dried with anhydrous $MgSO_4$. After solvent removal, the product was further purified by recrystallisation in petroleum ether. Yield (70%); ^{1}H NMR ($CDCl_3$; δ ppm): 7.17 (s, 4H, Ar), 2.057 (s, 12H, -CH_3).

Scheme 1: Reaction Condition of ATRP of Acrylamide

SYNTHESIS OF CONTROLLED POLYMER BY ATRP METHOD: POLY (ACRYLAMIDE)

Glycerol-water (1:1), Cu(I)Br (0.02869g, 0.2 mmol) and 2, 2’-bipyridyl (0.078g, 0.5 mmol) were charged into three necked 100 mL reaction flask, and the reaction mixture was bubbled with purified N_2 for 10 minutes. Solid acrylamide (0.710g, 10 mmol) was added with stirring, and the mixture was again purged with N_2 continuously and polymerization was started with the addition of the degassed solution of 1,4-bis (2-bromo *iso*butyryloxy) benzene (0.0816g, 0.2 mmol). Reaction was carried out for 24 h on oil bath and temperature was maintained at 130 ºC. 5 ml of aliquot was taken at desired time to check the conversion and rate of polymerization. The deactivated complex of copper was removed from aliquot with the help of basic alumina column and further polymer was precipitated in pure methanol. Yield (65%)

RESULT AND DISCUSSION

The terminal bromide bi-functional group containing ATRP initiator was synthesized at 0 °C in DMF and the product was characterized by ^{1}HNMR. Furthermore, the bromide terminated well controlled poly(acrylamide) was synthesized by using atom transfer radical polymerization process in the presence of BiBB initiator, catalyst (Cu(I)Br) and bpy ligand in glycerol and water solvent mixture at 130°C as illustrated in scheme-1. The conversion of monomer to polymer was good to retain a degree of chain end functionality. Initiator, catalyst (Cu(I)Br) and bipyridyl ligand (bpy) were used to synthesize the polymer at 130°C (scheme-2) in the ratio 1:1:2.5 respectively. The poly(acrylamide) terminated by Br was precipitated in excess of methanol and finally poly(acrylamide) was purified by passing it through short alumina column to remove copper(II)bipyridyl complex. The conversion of monomer to polymer was determined by ^{1}HNMR using the following equation:

$$\%C = \frac{\text{Weight of polymer formed in the aliquot}}{\text{weight of monomer charged in the aliquot}} \times 100 \qquad \text{equation 1}$$

The synthesis of Br terminated poly(acrylamide) was supported by ^{1}HNMR analysis, the appearance of singlet at δ1.15 ppm, singlet at δ7.06 ppm, in the spectrum of poly (acrylamide) (fig.2(b)) of $-CH_3$ and Phenyl, respectively. The appearance of peaks at □δ□6.085-6.186 ppm (triplet, broad, 1H) for the -CH-Br, δ4.441-4.511 ppm (doublet, broad, 46H) for the –CH of repeating unit, δ 3.301- 3.556 ppm (quartet, broad, 94H) for the $-CH_2$ of repeating unit. The appearance of these peaks supports the formation of polymerization of acrylamide by ATRP method.

Monomer conversion was determined by using the formula given in equation-1 and was about 65% and observed molecular weight Mn(4849) was higher than the theoretical molecular weight (2716), and under the same experimental condition using BiBB initiator resulted the oligomers of molecular weight(Mn) around 792 at about 1% monomer conversion.

$$\mathrm{Mn}_{\mathrm{NMR}} = M_{BiBB} + M_{ACM} \times \frac{\left(\dfrac{\text{Sum of methylene proton integral}}{\text{Number of methylene proton}}\right)}{\left(\dfrac{\text{Sum of end group proton integral}}{\text{Number of protons in end group}}\right)} \qquad \text{Equation -2}$$

$$\mathrm{Mn}_{\mathrm{Theo}} = \frac{[\mathrm{ACM}]_0}{[\mathrm{BiBB}]_0} \times \mathrm{X}_{\mathrm{ACM}} \times \mathrm{M}_{\mathrm{ACM}} + \mathrm{M}_{\mathrm{BiBB}} \qquad \text{Equation -3}$$

Low monomer conversion to polymer in this case may be due to the more stable and less reactive tertiary carbon centered free radical derived from BiBB. The high deviation from the theoretical of molecular weight one even at higher monomer conversion is due to the less initiator efficiency. Thus, the polymerization is more controlled at this temperature

DETERMINATION OF KINETICS OF REACTION

In order to check the livingness of the polymerization of ACM by ATRP process, the kinetic study was carried out at 130°C using BiBB initiator with molar ratio [ACM]: [Ini]: [Cu(I)Br]: [bpy] = 50:1:1:2.5. Figure 3 shows the plot of the monomer conversion (%) and $ln[M_o]/[M_t]$ verses time. Monomer conversion increases almost linearly up to 65%. The corresponding plot of $ln\ [M]_o/[M]_t$ verses time is linear with approximate 30 minute induction time. The first order monomer conversion rate was followed up to 65% conversion. Figure 4 shows the plot of Mn verses monomer percentage conversion, which reveals that molecular weight increases linearly with increase in conversion, but observed molecular weight drifted gradually from the corresponding theoretical values with increase in conversion. This result indicates that the propagating radical species concentration decreases slowly with increase in conversion. It is due to the loss of considerable chain transfer reaction to monomer.

TABLE 1:

Experimental Conditions and Properties of reactions by Normal ATRP Using BiBB as Initiator

[ACM]=10 mmol/L, [Cu (I) Br] =20 X 10^{-3} mmol/L, [BiBB] =20 X 10^{-3} mmol/L, [L] =50 X 10^{-3} mmol/L, Temperature=130^0C, Time= 24 hr, Solvent =Glycerol/water (1/1= v/v) for ATRP process

Conv.	Time(h)	ln[M0/Mt]	$Mn_{(theo)}$	Mn,NMR	DP
1	0.5	0.01005	444	792	0.5
5	3	0.05129	586	1046	2.5
12	6	0.12783	834	1489	6
35	12	0.43078	1651	2947	17.5
50	18	0.69315	2183	3898	25
65	24	1.04982	2716	4849	32.5

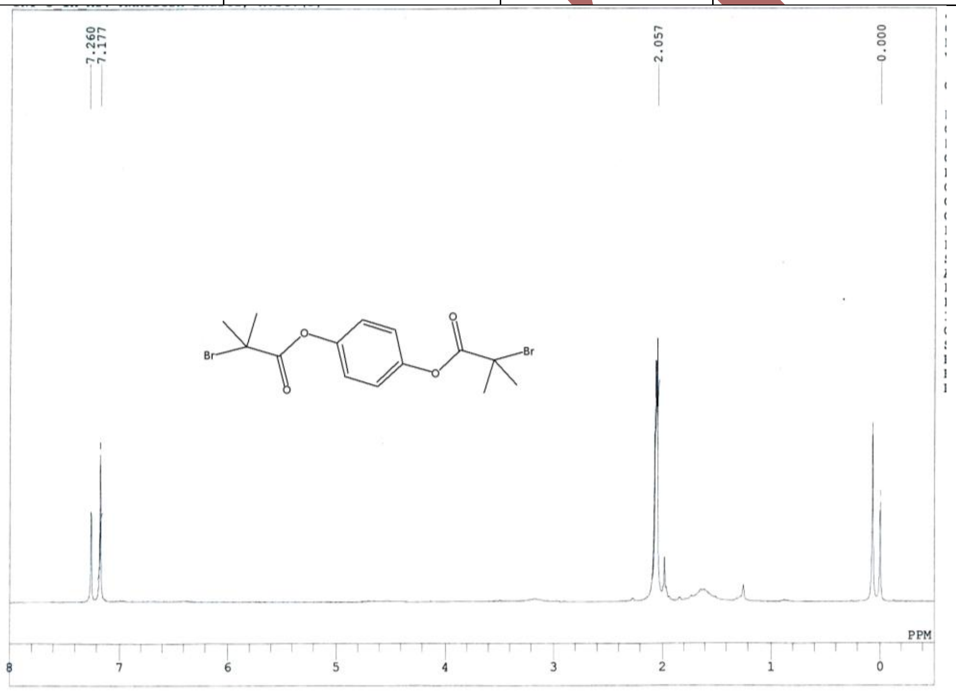

Figure 1: 1H NMR of 1,4-bis (2-bromo *iso*butyryloxy) benzene (a bi-functional initiator)

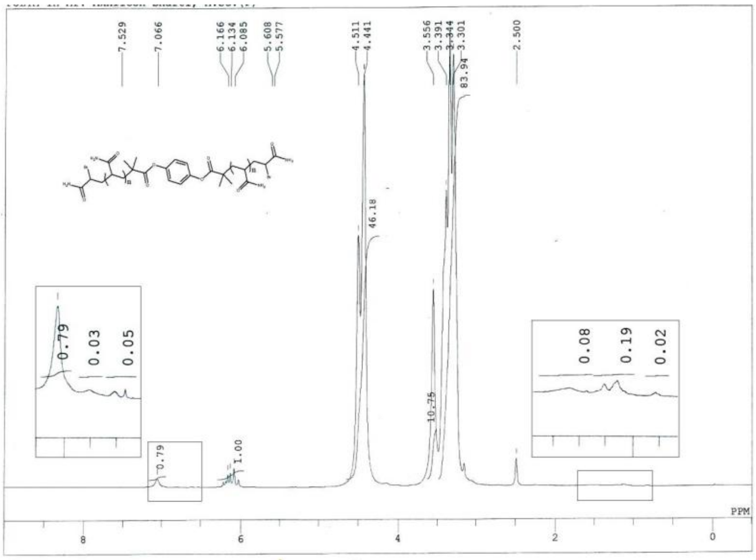

Figure 2(b): 1H NMR of Poly(Acrylamide) by 1,4-bis (2-bromo *iso*butyryloxy) benzene

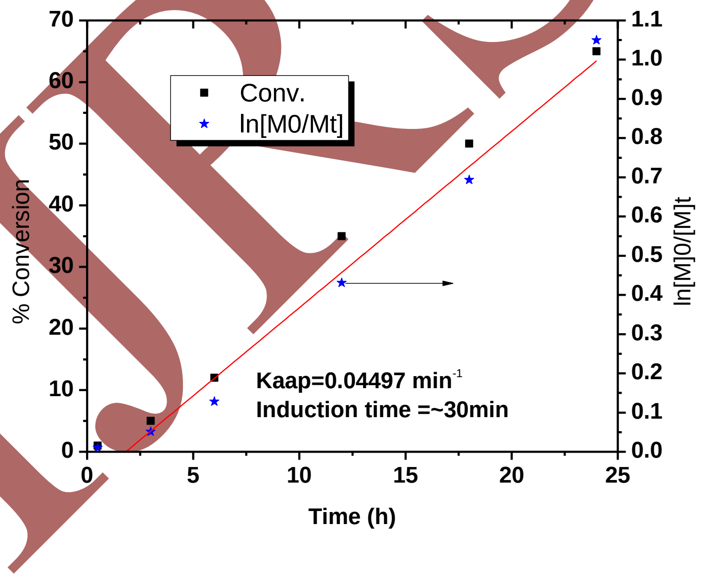

Figure 3: First-order kinetic plots for the ATRP polymerization of ACM

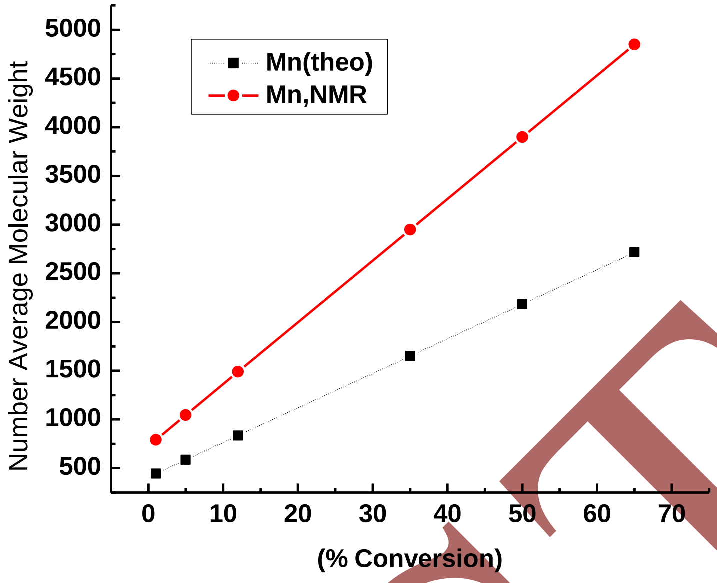

Figure 4: Number average molecular weight vs. % conversion plot

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