Rheological Properties and Conformation of Tomato Paste Pectins, Citrus and Apple Pectins

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- ABSTRACT -

Rheological properties of dilute and concentrated solutions of watersoluble, alcohol-precipitated tomato pectins from hot break and cold break tomato paste as well as alcohol-precipitated commercially available apple and citrus pectins were studied. Superposition of rheological data was possible when n_{sp} was plotted vs c[η] and when η/η_o was plotted vs $\tau \dot{\gamma}$ The slope of n_{sp} vs cMw plot and the limiting slope of η/η_o vs ($\tau \dot{\gamma}$ suggested that citrus, apple and hot break tomato pectin had random coil conformation while cold break tomato pectin had a more rigid conformation. Tomato processing had significant influence on the chain length and rheological properties of tomato pectins.

INTRODUCTION

Consistency is a major quality factor in plant purees and pastes such as tomato paste (USDA, 1953). Understanding of the factors involved in viscosity development as well as the major biochemical components responsible for viscosity in fruits and vegetables such as tomatoes could lead to the breeding of plant fruits rich in those ingredients or the development of engineering processes designed to preserve those biopolymeric components, known to enhance viscosity. This in turn would be translated into more economical purees and pastes such as tomato paste.

There has been considerable effort towards this objective. Alcohol insoluble solids (AIS) were shown to be responsible to a large extent for the consistency of pureed tomato products (Kertesz and McColloch, 1950). By treating alcohol-insoluble solids from fresh tomatoes with the enzymes, pronase, cellulase and pectinase, Brown and Stein (1977) attempted to show the importance of proteins, pectins and cellulose in tomato paste viscosity. Their results showed an increase in viscosity after pronase treatment while cellulase and pectinase caused a decrease in viscosity. Brown and Stein (1977) also showed that AIS were highest in the pear-shaped tomato cultivars and lowest in the round tomato cultivars.

Foda and McCollum (1970) also in their studies on the viscosity of tomato juice showed that tomato cellulose as well as water-soluble solids significantly affected viscosity of tomato juice. They also found that the high molecular weight polymers associated with the insoluble solids contributed quite significantly to viscosity as expected.

Luh and Daoud (1971) reported on the effect of break temperature and holding time on pectin and pectic enzymes in tomato pulp. The gross viscosity and serum viscosity of the canned tomato pulp increased as break temperature increased and was related to total pectin of the tomato pulp as well as the total pectin in the serum which also increased as the break temperature increased. Viscosity and total pectin also increased as holding time increased. This was thought to be due to the inactivation of pectic enzymes at high break temperature and longer holding times. The same phenomenon was observed and reported in more detail by Sherkat and Luh (1976) and

Authors Chou and Kokini are with Rutgers Univ., New Jersey Agricultural Experiment Station, Food Science Dept., Cook College, New Brunswick, NJ 08903. was explained by the formation of pectic acids, oligouronic and galacturonic acids at the lower temperatures since pectic enzymes would deesterify and depolymerize pectin leading to the small molecular weight acids. The retention of pectin in canned and frozen tomato pastes at 104.4°C (220°F) break temperature was 50% higher than that at break temperature of 65.6°C (150°F). The retention of protopectin at 104.4°C (220°F) break temperature is 100% higher than that at 65.6°C (150°F).

Seventy-eight percent or more of pectin is composed of α -1,4 linked D-galacturonate units with varying degrees of methylated carboxyl groups. The remainder of pectin is composed of the neutral sugars, L-arabinose, D-galactose and L-rhamnose, D-glucose, D-mannose and D-xylose (Baig and Burgin, 1982). Rees and Wight (1971) and Rees (1977) have suggested that polygalacturonic acid is a flat helical ribbon and pectins are blocks of these polygalacturonic units separated by rhamnose inserts acting as tees for segments of the various neutral sugars. The polygalacturonic acid could be considered to be a rod in solution whereas pectins are segmented rods with flexibility at the rhamnose tees. Fishman et al. (1984) found that radii of gyration depended on such variables as mobile phase, method of purification, chemical modification and methoxyl content.

The molecular size of tomato pectic substances, extracted according to their solubility in water, 0.2% ammonium oxalate, 0.05N hydrochloric acid and 0.05N sodium hydroxide, was found to be heterogeneous with the majority having a molecular weight of 2×10^5 (Stein and Brown, 1975) using gel filtration.

Luh et al. (1984) found that the molecular weights of pectinic acids isolated from fresh tomatoes of six cultivars ranged from 26,800 to 7,870. When tomato paste was produced from these cultivars, the weight average molecular weight decreased substantially ranging from 17,900 to 5,300. Polydispersity factors (Mw/Mn) in pectic substances were around 11 suggesting a large degree of polydispersity (Smith and Stainsby, 1977). Polydispersity is known to shift the transition from Newtonian behavior to lower shear rates, however, at sufficiently higher shear rates the behavior becomes similar for all distributions.

The objectives of this research were (1) to elucidate the effect of hot break and cold break processing on the chain length and on the dilute and concentrated rheological properties of the water soluble fraction of tomato pectic substances in a pH buffer system simulating tomato paste acidity, and (2) to compare rheological properties of hot break and cold break water soluble tomato paste pectins to commercially available apple and citrus pectins.

MATERIALS & METHODS

HOT BREAK AND COLD BREAK tomato pastes which had total solids of 26% and 46%, respectively, were supplied by Campbell Soup Company. Citrus pectin and D-galacturonic acid, used as a standard, were purchased from Sigma Chemical Company (St. Louis, MO). Apple pectin manufactured by Herbstreith KG., West Germany, was a generous contribution from Harcros, Inc.

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Extraction of water-soluble pectic substances from tomato paste

Water-soluble tomato pectin was extracted from hot break and cold break tomato paste. First, two parts of deionized distilled water were mixed thoroughly with one part tomato paste for 15 min, followed by continuous centrifugation at 15,000 rpm (7,500g) using Sharples AS-16 continuous centrifuge. The supernatant was filtered through Whatman No. 4 filter paper to remove trace fibers and cracked seeds. The filtrate was mixed thoroughly with an equal volume of 2-propanol to precipitate the pectic substances which were isopropanol-insoluble. After 15 min stirring, the suspended solids in water-isopropanol were separated using continuous centrifugation at 15,000 rpm (7,500g). The resulting tomato colored gel was dissolved in deionized water and then freeze-dried. The yield of freeze-dried hot break tomato pectin on dry solid basis was 7% and that of cold break tomato pectic was 2.9%.

Removal of carotenoids in tomato pectins

The red color in tomato paste is mostly due to the carotenoids, lycopene (87%) and β -carotene (7%) (Ferrari and Benson, 1961). To remove these carotenoids, the method of Liu and Luh (1979) was used. A solution of two volumes acetone/one volume hexane was used to extract carotenoids from the colored pectin dispersion in water. After color removal was complete, the solvent was evaporated using vacuum evaporation at 26°C. The resulting white mass was dissolved in water and freeze-dried.

Preparation of buffers

Buffers at pH values of 2.6, 4.6 and 6.6 were prepared for hot break tomato paste pectin using citrate-phosphate buffers (Dean, 1985) to simulate variations around the natural pH of 4.6 for hot break paste, pH was measured using an Orion digital Ionanalyzer model 701 A. Citric acid monohydrate, potassium hydrogen phthalate and reagent grade HCl, dibasic sodium phosphate were purchased from Fisher Scientific, (Springfield, NJ). Buffers at pH of 2.3, 4.3 and 6.3 were used in the case of cold break tomato paste pectin to simulate variations around the natural pH of 4.3 for cold break paste. To prepare a buffer solution at a pH of 2.3 phthalate-hydrochloric acid buffer (Dean, 1985) was used since the pH of 2.3 was beyond the range of the citrate-phosphate buffer.

Rheological measurements

Capillary viscosity measurements were conducted by using size 50, and 100 Cannon Fenske capillary viscometers. Densities of solutions were measured using a 25 mL Dormax Gay-Lussac type pycnometer at 24°C using a water bath. Viscosities measured in this way were converted to specific viscosities (η_{sp}) using:

$\eta_{sp} = (\eta - \eta_s)/\eta_s$

where, η is the viscosity of solution, and η_s is the viscosity of solvent, intrinsic viscosity was calculated using:

$$[\eta] = \lim_{c \to 0} (\eta_{sp})/c$$

where c is the concentration of the solution. The slope of n_{sp} vs c plot in the dilute solution region gives a first estimate; extrapolating to zero concentration a plot of η_{sp}/c vs c in very dilute solution region was used to confirm the results obtained from the first technique. (Huggin's method) (Morris and Ross-Murphy, 1980)

Steady shear viscosity measurements were conducted using the cone and plate geometry of a Rheometrics Fluids Rheometer in the shear rate range of 0.1 to 100 sec⁻¹ A cone with an angle of 0.0196 radians and a gap size of 50 microns was used. All measurements were conducted at room temperature $(23-25^{\circ})$.

Small amplitude dynamic oscillatory measurements were performed using the cone and plate geometry of the Rheometrics Fluids Rheometer. Linearity of complex viscosity was observed in the strain range of 0.1 to 100%. A strain of 20% was selected as being optimal for best resolution of the stress signal. Storage moduli G' which is the elastic component of the sample solution and loss moduli G" which is the viscous component of the sample solution were measured in the frequency range of 0.1 to 100 scc⁻¹.

Measurement of molecular weight

Gel permeation chromatography (GPC) using Pharmacia Sephacryl S-300 and S-500 resins was conducted to determine the molecular weight of pectin samples. Citrate-phosphate buffer of pH 4.6 was used as solvent system for citrus, apple and hot break tomato pectins. Citrate-phosphate buffer of pH 4.3 was the solvent for cold break tomato pectin. GPC column of 1.5×40 cm was purchased from BRL Co. The bed volume was 53 cm³. A Waters HPLC pump was used as the solvent delivery system to ensure the steady flow rate of 0.5 mL/min. A LKB 2112 Redirac fraction collector (Gaithersburg, MD) was used to collect the eluent at one min intervals. Blue dextran from Pharmacia was used to determine the void volume and dextran T-10, T-40 and T-70 (Pharmacia) were used to generate the universal calibration curve of $\log[\eta]\overline{Mw}$ vs retention volume (v) for the particular packed column as shown in Fig. 1 (Kato et al., 1983). The anthrone method of Troy and Eugene (1953) was used to determine the concentration of dextran in solution. The uronide content in the eluent was measured using the carbazole method modified by Bitter and Muir (1962).

Determination of uronide in pectin

Uronide was measured using the carbazole method modified by Bitter and Muir (1962). In this procedure 3 mL 0.02 M sodium tetraborate (Sigma Chemical) in 93% sulfuric acid was added to 0.5 mL sample solution in an ice bath, followed by mixing with a Vortex mixer. The mixture was heated in a boiling water bath for 10 min. After cooling down to below 20°C in the ice bath, 0.1 mL 0.1% carbazole (Eastman Kodak Co.) in ethanol was added and mixed thoroughly by Vortex again. The solution was heated again in boiling water bath for 15 min and its absorbance was measured at 530 nm after cooling to room temperature. Uronic acid content was obtained by comparison with a standard plot.

Determination of degree of esterification

Degree of esterification (D.E.) was determined using the titration method of Schultz (1965) and Schweiger (1965). Ten milliliters 1% pectin solution were titrated with 0.1N NaOH (Titration A). Twenty milliliters 0.5N NaOH were added for 30 min to de-esterify the pectin and 20 mL 0.5N HCl were added to exactly neutralize the NaOH. This mixture was titrated with 0.1N NaOH (Titration B), using phenolphthalein as indicated. The degree of esterification can be calculated through the following equation:

D.E. =
$$[B/(A+B)] \times 100\%$$

RESULTS & DISCUSSION

Characterization of pectic systems

Degree of esterification, intrinsic viscosities, weight average molecular weights (\overline{Mw}) , number average molecular weights (\overline{Mn}) and, polydispersity factors $(\overline{Mw}/\overline{Mn})$ for all four pectins studied in pH 4.6 buffer are shown in Table 1. Intrinsic viscosities obtained using both methods were within 6% error. Tomato pectin from hot break tomato paste, citrus and apple pectins, all had similar intrinsic viscosities. Tomato pectin from cold break tomato paste had a value three times lower than that of tomato pectin from hot break paste. This confirmed earlier studies which suggested that cold break processing affected the chain length of tomato pectins through the action of pectic enzymes. These observations were also supported by the magnitude of Mw and Mn values. In parallel with intrinsic viscosity values Mw and Mn values for hot break tomato paste, citrus and apple pectins were similar in magnitude. Mw ranged from 2.29×10^5 for tomato paste (hot break) pectin to 1.04×10^5 for citrus pectin and Mn values from 1.48×10^4 for tomato pectin to 8.22×10^3 for citrus pectin. The Mw value of cold break tomato pectin (approx. 6000) was 38 times lower than that of tomato pectin obtained from hot break tomato paste. The \overline{Mn} value was 440, consistent with the \overline{Mw} value obtained. Mw/Mn ratios for all four pectins showed a similar, high degree of polydispersity with actual values ranging from 15.5 for tomato (hot break) pectin to 12.65 for citrus pectin. This is useful because the results are not clouded by differences in degree of polydispersity.

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Fig. 1 – <u>(a)</u> Calibration curve: $log[n]\overline{Mw}$ is plotted vs elution volume(v) for Sephacryl S-500 packed column; (b) Calibration curve : $log[n]\overline{Mw}$ is plotted vs elution volume(v) for Sephacryl S-300 packed column.

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		[η] m³/kg				
Pectin	D.E.	Huggins ^a	η _{sp} vs c ^b	₩w×10 ^{~5}	Mn×10-5	Mw/Mn
Tomato (hot break)	62	0.34	0.36	2.29	0.1477	15.50
Tomato (cold break)	28.5	0.11	0.09	0.06	0.0044	13.64
Citrus	63	0.43	0.48	1.04	0.0822	12.65
Apple	49.5	0.26	0.28	2.23	0.15	14.87

^aHuggins' method of extrapolating n_{sp}/c vs c to zero concentration.

^bSlope of n_{sp} vs c plot.

Intrinsic viscosity is a measure of the hydrodynamic volume occupied by a molecule and the nondimensional parameter $c[\eta]$ can be taken as a measure of the extent of overlapping between polymer molecules. The role of the parameter $c[\eta]$ can best be understood using the Huggins equation:

$$\eta_{\rm sp} = c[\eta] + k'[\eta]^2 c^2$$

When the second term is negligible as in the case of dilute solutions a plot of η_{sp} against $c[\eta]$ will be linear. At high concentration and molecular size the second term comes into play and a nonlinear plot results. When η_{sp} is plotted vs $c[\eta]$ on log-log coordinates, this curve can be approximated with two straight lines (Fig. 2). The transition from dilute to concentrated solution in this case occurs at a $c[\eta]$ value around 6. This is consistent with Morris and Ross-Murphy's (1980) observations which suggested that the transition should be at $c[\eta]$ values around 4.5. Frisch and Simha (1956) on the other hand suggested that the onset of coil overlap would start around values of $c[\eta] = 1$. This was not observed in this study. It must be noted that even though $c[\eta]$ provides an excellent superposition of zero-shear Newtonian viscosity data, it does not account for differences in polymer conformation (Baird and Ballman, 1979). It is not known, however, whether chain stiffness will promote the onset of entanglements at much lower c[n] values than flexible chain polymers (Baird and Ballman, 1979).

A second way of characterization and superposition of viscosity data is by plotting $\log \eta_{sp}$ vs $\log cMw$. Only molecules with the same approximate shape and conformation will superimpose. This is shown in Fig. 3 for all four pectins. Each pectin was somewhat different and a complete superposition was not possible. For flexible random coil the slope of the log η_{sp} vs log cMw curve would give exponents around 3.5 while stiffer chained molecules should give slopes in the neighborhood of 8. Apple, citrus and tomato pectins obtained from hot break tomato paste all have slopes around 3.3 while tomato pectin obtained from cold break tomato paste had a slope of 5.0 suggesting a stiffer chain. Baird and Ballman (1979) reported slopes around 8.8 for poly-p-phenyleneterephthalamide, a molecule known to behave as a rigid rod (Kwolek, 1972). The slope obtained for cold break tomato paste pectin, therefore, suggested that while the molecule was much stiffer, it still maintained some flexibility.

Steady shear viscosity data of biopolymers obtained from steady shear measurement can be superimposed if η/η_o is plotted vs $\tau \dot{\gamma}$ where τ is a characteristic relaxation time, η_o is the zero shear viscosity and $\dot{\gamma}$ is shear rate. For flexible monodisperse random coiled molecules the Rouse relaxation time provides a good approximation in the semi-dilute solution region:

$$\tau_{\rm R} = (6/\pi^2)[([\eta]\eta_{\rm s}M)/({\rm RT})]$$

where $[\eta]$ is intrinsic viscosity, η_s is solvent viscosity, M is the molecular weight of pectin. R is gas constant and T is absolute temperature.

For polydisperse systems like the pectins studied in this work an experimental relaxation time equal to the inverse of the shear rate where η/η_0 was equal to 0.9 was selected to have a consistant transition of zero shear viscosity and non-Newtonian region which will lead to the estimation of relaxation time. This is consistent with earlier approximation of relaxation time (Graessley, 1974). These results are shown in Fig. 4 for three concentrations of citrus pectin, two concentrations of apple pectin, tomato pectin from hot break paste. The data



Fig. 2—Specific viscosity vs c[n] for hot break tomato pectin (HBP), cold break tomato pectin (CBP), citrus and apple pectins.

in this form superimposed very nicely and covered three decades of reduced shear rates. Data from cold break pectin did not closely superimpose on the curve. The slope of the limiting non-Newtonian region was equal to -0.6 as expected from random coil molecules.

Effect of processing and pH on rheological properties of tomato paste pectin

The pH of pectin systems is known to be critical in several ways. The presence of free carboxyl groups causes pectin solutions to display an acidic pH. When subjected to acidic conditions, the glycosidic bonds and the methyl ester linkages of pectin are prone to hydrolysis leading to galacturonic acid (Nelson et al., 1977). On the other hand pH starting from values in the range of 6.8 (Albersheim, 1959) may result in β -elimination and depolymerization. The role of these changes on tomato pectins need to be understood for optimal viscosity generation. Specific viscosity vs concentration for buffer solutions with pH 2.6, 4.6 and 6.6 are shown in Fig. 5. The specific viscosity in the dilute solution was similar for all pH values but in the more concentrated region there was a pH effect. Solution viscosity was optimal at a pH of 4.6 and lower at both pH 2.6 and 6.6. This can be explained by the fact that in the case of HBP the degree of methylation was 62%. In this case the degree of esterification seemed to play a significant role. Fishman et al. (1984) have shown that the radius of gyration of pectin is highest for pectins with a degree of esterification around 57%. It is conceivable that the optimal degree of esterification for viscosity in tomato pectin occurs around a pH of 4.6 where the specific viscosity is highest. The lower



Fig. $3 - n_{sp}$ vs c \overline{Mw} for hot break tomato pectin (HBP), cold break tomato pectin (CBP), citrus and apple pectins.



Fig. $4-N/n_o vs \tau\gamma$ for hot break tomato pectin (HBP), citrus and apple pectins.

viscosity at a pH of 2.6 can be explained by the fact that some deesterification could conceivably occur at this pH because of acid conditions (Nelson et al., 1977) resulting in a lower radius of gyration for pectin and, therefore, a lower viscosity. The lower viscosity at a pH of 6.6 could be due to the initiation of small amounts of β -elimination.

A similar graph for cold break tomato paste pectin is shown in Fig. 6. The change in viscosity with respect to pH in the case of cold break tomato paste pectin was much smaller than in the case of hot break tomato paste pectin. The degree of esterification of cold break pectin is in the 28.5% range. In the low pH range any deesterification would not cause a significant conformational change while at the pH of 6.3 pectins of low degree of esterification are known to be more resistant to degradation under alkaline conditions (Nelson et al., 1977).

The concentration and shear rate dependence of pectin from hot break tomato paste is shown in Fig. 7 and that for cold

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CONFORMATION OF PECTINS



CONCENTRATION(%)

Fig. 5—Specific viscosity vs concentration for tomato pectins from hot break tomato paste as a function of pH.



Fig. 7—Viscosity vs shear rate of tomato pectin from hot break tomato paste at pH 4.6 as a function of concentration.





Fig. 6–Specific viscosity vs concentration for tomato pectins from cold break tomato paste as a function of pH.

break tomato pectin is shown in Fig. 8. In Fig. 7 steady shear viscosities of 2, 3 and 4% of hot break tomato paste pectin is plotted vs shear rate. At the concentration of 2%, the solution

Fig. 8—Viscosity vs shear rate of tomato pectin from cold break tomato paste at pH 4.3 as a function of concentration.

was essentially Newtonian and did not show any significant shear thinning. On the other hand, at a concentration of 3% and below the shear rate of approximately 10 sec⁻¹, it was

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Fig. 9–Zero shear viscosity vs concentration for hot break tomato paste pectin (HBP) and cold break tomato paste pectin (CBP).

essentially non-Newtonian. The shear rate dependence at 4% was essentially similar except that the onset of non-Newtonian behavior had shifted to a smaller shear rate around 3 sec⁻¹.

For cold break tomato paste pectin in Fig. 8 on the other hand the concentration dependence of viscosity is markedly different. At very high concentrations of 15% and 20%, the dispersions were largely Newtonian in the shear rate range studied while at 30% there was a slight non-Newtonian behavior. This was again due to the smaller chain length of cold break tomato paste pectin.

Concentration dependence of viscosity can better be exemplified by plotting the logarithm of zero-shear viscosity vs concentration in the concentrated region. Zero-shear viscosity corresponds to the Newtonian region of each flow curve shown in Fig. 7 and 8. The plot of log η_0 vs C is shown in Fig. 9 It can be seen from Fig. 9 that the slope of the line for HBP is equal to 0.060 while that for CBP is equal to 0.0084. This result further demonstrated that HBP viscosity increased much more sharply with concentration than cold break tomato paste pectin did. Further insight in reference to the viscoelastic properties of pectin solutions can be gained using small amplitude oscillatory measurements.

Measurements carried out at 20% strain for HBP are shown in Fig. 10. In this figure G' and G" were plotted vs frequency in rad/sec for 1.5, 2.5 and 4.5%. For each concentration G" was larger than G' suggesting more of a fluid-like behavior throughout the whole frequency range of 0.1 to 100 sec⁻¹. Furthermore, the fact that G" remained larger than G' throughout the whole concentration and frequency range suggested that only weak entanglements were formed which resulted in a weak temporary network.

In the case of cold break pectin in Fig. 11 the same conditions are observed for concentration of 30%. At the concentration of 40%, G' is initially larger than G" suggesting the formation of a weak filled structure which breaks down with increasing frequency. This is possible if one considers that at this high concentration the large concentration of short chain



Fig. 10—Dynamic viscoelastic properties of tomato pectin from hot break tomato paste at 1.5, 2.5 and 4.5% concentration in pH 4.6 buffer.



Fig. 11 – Dynamic viscoelastic properties of tomato pectin from cold break tomato paste at 30, 40 and 50% concentration in pH 4.3 buffer.

pectins would lead to extensive aggregation resulting in a weak network similar to what would be observed in tomato paste itself. This weak network effect was also seen for 50% and G' was larger than G'' at a wider range of frequencies as would be expected at the larger concentration where crowding was more pronounced.

In conclusion superposition of rheological data was possible when η_{sp} was plotted vs $c[\eta]$ and when η/η_o was plotted vs τ $\dot{\gamma}$. Plotting η_{sp} data vs CM_w on the other hand clearly demonstrated that each pectin system is somewhat different even though citrus, apple and tomato pectins for hot break paste all demonstrated random coil type behavior, tomato pectin from cold break tomato paste on the other hand showed more rigid behavior. Furthermore, it was shown that tomato processing had drastic influence on the chain length and resulting conformation of tomato paste pectins. The nature of the pectin after processing also influenced the viscosity imparting characteristics as a function of pH, concentration and shear rate.

SYMBOLS

concentration(%)

с

G' storage modulus(dyne/cm²)

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CONFORMATION OF PECTINS

G″	loss modulus(dyne/cm ²)
Mw	weight average molecular weight(g/mole)
Mn	number average molecular weight(g/mole)
η	solution viscosity(poise)
ηο	zero shear viscosity(poise)
[ŋ]	intrinsic viscosity(m ³ /kg)
η_s	solvent viscosity(poise)
η_{sp}	specific viscosity
τ	relaxation time(sec)
γ	shear rate(sec ⁻¹)

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