

Influence of Tacticity and Sorbed Water on the Material Properties of Poly(*N,N'*-Dimethylacrylamide)

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Synopsis

The effects of variation in tacticity on the thermal, morphological, stress-strain and stress-relaxation properties (both in the dry state and 140°C, and at a RH of 72% and ambient temperature) were evaluated for a series of homopolymers of poly(*N,N*-dimethylacrylamide). In the range of 19 to 23% tacticity (isotactic content), a fundamental change in the level of crystallinity and morphology occurs for this series of polymers which in turn greatly affects the above-mentioned properties. Below 19% tacticity, the polymers are amorphous, but above 23% they are distinctly semi-crystalline. Sorbed water plasticizes all these polymers, but the influences of the water on the stress-strain properties is greatest for the amorphous polymers, where the relative sorption of water is also highest.

INTRODUCTION

The majority of past research directed at determining the effect of the variation in tacticity on material properties has been concentrated on hydrophobic polymers such as polypropylene¹⁻⁵ or polystyrene.^{6,7} There has also been some work reported on the influence of tacticity on properties of some polar and hydrophilic polymers. For example, the effect of tacticity on the thermal behavior⁸ and the glass transition temperature⁹ of poly(methyl methacrylate) has been investigated. The dependence of the dynamic mechanical behavior on tacticity of poly(alkyl α -chloroacrylates) has also been discussed in detail.¹⁰ In these hydrophilic systems, not only the tacticity, but also the amount of sorbed water affects their material properties. Although there have been some investigations relating tacticity and water sorption,¹¹ studies in which both the effects of tacticity and water uptake are considered with respect to properties are limited. For example, the effect of water and tacticity on the glass transition of poly(2-hydroxyethyl methacrylate) has been reported recently.¹² The influence of tacticity on mechanical properties of aqueous poly(vinyl alcohol) gels¹³ has also been briefly discussed.

In this article, we wish to report the effect of the variation in tacticity and percent water sorption on the material properties of a series of homopolymers of *N,N'*-dimethylacrylamide (PDMA). These extremely hydrophilic polymers were prepared from anionic polymerization of the monomer in various solvents or solvent mixtures^{14,15} to achieve isotacticity ranging from 14 to 41%. The thermal, mechanical, and optical properties of this series of polymers, ranging from completely amorphous to partially crystalline, are reported. The equilibrium water uptake and its effect on the mechanical properties of PDMA are

also discussed. Preliminary work on the rate of water sorption is also reported.

EXPERIMENTAL

Preparation and Characterization of Samples. Polymers of varying tacticity (% isotactic triads) were prepared from the polymerization of *N,N'*-dimethylacrylamide in various solvents and solvent mixtures using *sec*-butyllithium as initiator. The exact conditions of preparation have either been published¹⁴ or will be published later.¹⁵ The tacticity of the polymer samples was determined by solution NMR studies.¹⁴ The intrinsic viscosity of the samples was measured in methylene chloride. For a given isotacticity, more than one polymer was prepared. Hence, each polymer will be designated by giving its percent tacticity followed by the value of intrinsic viscosity. For example, PDMA/14/2.08 designates a polymer with 14% isotactic content whose intrinsic viscosity is 2.08 dL/g. Films of the samples were made by casting 2% solutions from methylene chloride on a Teflon surface. After drying under ambient conditions, the films were further dried in a vacuum oven for over a week at 80°C before any measurement was taken. The glass transition and the melting temperature of the polymers were obtained via DSC. The heating rates are given in Table I.

Since the polymers were hydroscopic, to eliminate water it was necessary to heat the sample to 180°C in the DSC followed by cooling and then obtain the thermogram immediately thereafter in a second scan (Fig. 1). The low-angle light scattering H_v patterns and the optical micrographs were obtained from the samples cast from methylene chloride; similar samples were prepared for mechanical studies.

TABLE I
Characteristics of the Homopolymers of *N,N'*-Dimethyl Acrylamide

Polymer	^a % Isotactic Content	^a μ	^b [η]	^c T _g °c	^d T _m °c	^g T _d °c
PDMA/14/1.33	14	4.5	1.33	119	None	above 347
PDMA/14/2.08	14	4.2	2.08	118	None	338
PDMA/18/3.85	18	5.5	3.85	121	None	344
PDMA/19/4.08	19	4.8	4.08	120	None	342
PDMA/23/1.86	23	7.6	1.86	120	278 ^e 312 ^f	345
PDMA/23/3.75	23	7.6	3.75	120	247 ^e 257 ^f	292
PDMA/28/1.28	28	10.3	1.28	119	309	330
PDMA/28/5.33	28	15	5.33	121	323	347
PDMA/39/1.70	39	14	1.70	117	312	327
PDMA/41/1.91	41	17.3	1.91	112	326	338

^a By NMR.

^b In methylene chloride.

^c Heating rate 20°C/min.

^d Heating rate 10°C/min.

^e Small peak.

^f Shoulder.

^g Decomposition temperature.

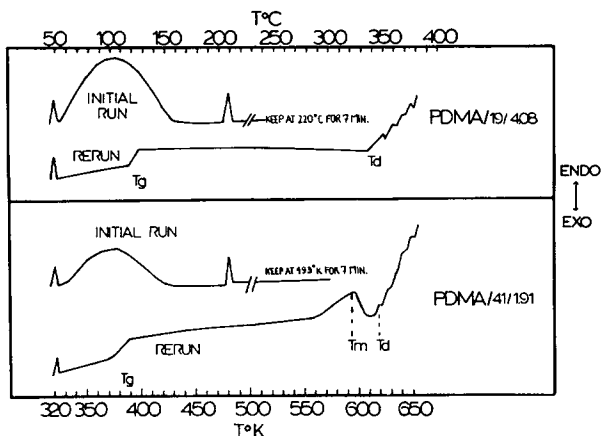


Fig. 1. DSC thermograms of an amorphous and a semicrystalline PDMA polymer. See text for details.

Equilibrium Water Sorption. The equilibrium water uptake of the samples was obtained in the following manner: a sample weighing around 0.1 g was cut and dried carefully in a vacuum oven for two days at 80°C. It was then immediately weighed to obtain the weight of the dry polymer, after which it was placed above a saturated aqueous solution of KNO_3 and NH_4Cl ($\text{RH} = 72\%$ at 20–25°C). The sample was then weighed again after a period of 24 h to obtain the water uptake.

Rate of Water Sorption. The diffusion coefficient D of water into the PDMA films was measured from the rate of water sorption. A polymer film was dried for at least 48 h in a vacuum oven at 80°C. It was then suspended from a thin wire in a Mettler balance (model H4) whose chamber was continuously flushed with a stream of air with relative humidity of 74% at ambient temperature. The original weight of the dry polymer was noted initially (time $t = t_0$), and subsequent weight gains were followed with time. The air with a relative humidity of 74% was produced by passing an air stream over several columns of water at $20 \pm 0.2^\circ\text{C}$. The saturated air was then warmed to ambient temperature (by passing through a copper coil) before it entered the sorption chamber (balance chamber). Circular films with diameter of 8–9 cm and thickness of 3–5 ml were used for this experiment. The diffusion coefficient D of water was obtained from the initial slope of the plot of $W_{\text{H}_2\text{O}}/W_{\text{H}_2\text{O}}^\infty$ vs. \sqrt{t}/l , using the relation $D = (\pi/16)(\text{slope}^2)$, where $W_{\text{H}_2\text{O}}$ and $W_{\text{H}_2\text{O}}^\infty$ are weight of water sorbed at time t and t_∞ , respectively, and l is the thickness of the film in cm.¹⁶

Stress-Strain. The stress-strain properties of the samples were measured on a Ladd tensile stage with an environmental chamber under two differing conditions: (a) at 140°C and dry conditions, and (b) ambient temperature and a relative humidity of 72%. In the first case, the measurement was carried out about 20°C above the glass transition temperature of the polymers. Below the glass transition temperature and in the dry state, all of the samples were brittle. However, plasticization by sorbed water vapor at 72% RH and ambient temperature causes this series of polymers to exhibit distinct differences in mechanical properties, as will be discussed. The stress-strain properties at 72% RH were determined by the following procedure: First, the samples were allowed

to equilibrate with the water vapor above a saturated aqueous solution of KNO_3 and NH_4Cl in a closed container. After this equilibration, a sample was removed from the container and rapidly mounted on the instrument, and then a chamber containing the same aqueous salt solution was placed around the sample. Elongation was started about 5–10 min after waiting to reach equilibrium vapor pressure. The rate of elongation was 15%/min with samples of 0.28 cm width and 1.0 cm effective length.

Stress-Relaxation. When a sample reached a 200% elongation in the stress-strain experiment, it was maintained at that elongation and the decay of stress was monitored with time. Plots of $f(t)/f(0)$ against $\log t$ are presented in Figs. 9 and 10, where $f(0)$ and $f(t)$ are force at time zero (i.e., the time when sample just reached 200% elongation) and time, t , thereafter, respectively.

RESULTS AND DISCUSSION

Characterization

A summary of the characteristics of the polymers are given in Table I. The percent isotacticity of the polymers changes from the lowest value of 14% to the highest of 41%. The tacticity is an important parameter of the polymer and, as discussed later, it strongly influences the crystallinity and morphology of the polymer. Since the Mark-Houwink constants are not known for this polymer, the absolute molecular weight of these polymers was not determined. But as seen on Table I, the intrinsic viscosities of the polymers were within the range 1.3–5.3 dL/g. In this respective viscosity range, the samples were brittle below the glass transition temperature. However, the mechanical properties of the samples above the transition temperature were quite satisfactory, indicating that molecular weight was above the critical value for entanglement formation.

The results of the DSC runs are also shown in Table I. Since the samples were hygroscopic, it was necessary to remove the water by heating the sample inside the instrument during the first run (see Fig. 1). The evaporation of water resulted in a broad endothermic peak between 50 and 150°C, after which the sample was further heated to 220°C and kept at this temperature for 7–8 min to ensure complete removal of water. After the sample was quickly quenched to 50°C (to minimize possible resorption of water), a second DSC thermogram was obtained. The glass transition was quite distinct in this rerun (Fig. 1). It has been reported that the DSC of an atactic PDMA prepared by free radical polymerization showed an endothermic peak in the range 155–185°C.¹⁷ The previous author assigned this peak to a melting phenomenon. However, it is more likely that this endotherm was caused by evaporation of the sorbed water as observed in the DSC behavior of our amorphous low-tacticity polymers. In the tacticity range of 14 to 28%, the glass transition temperature is approximately 120°C, changing very little, if at all. However, there is a noticeable decrease in the glass transition temperature with an increase in percent isotactic content perhaps at, but definitely above, 39%. In the sample with 41%, the glass transition temperature decreased to 112°C. A decrease in T_g with an increase in isotacticity has also been observed for poly(methyl methacrylate),^{8,9} poly(alkyl α -chloroacrylates),¹⁰ and poly(2-hydroxyethyl metacrylate).¹² It has been suggested that this is related to a difference in the intramolecular interactions and/or the chain stiffness of molecules of different tacticity.^{18,19}

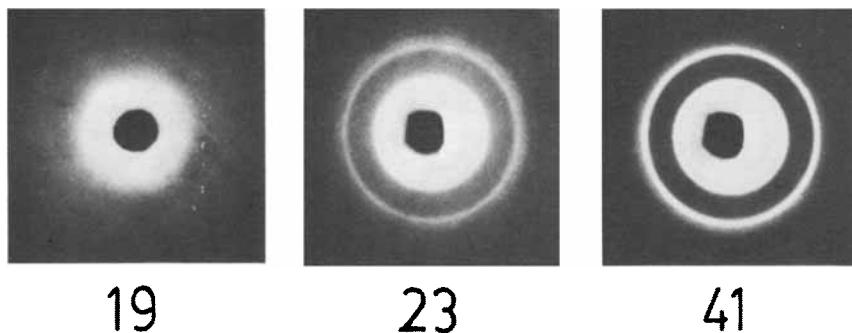


Fig. 2. WAX patterns of PDMA polymers of various tacticity. The percent tacticity is shown in the figure.

The thermal behavior of the polymers above T_g becomes particularly dependent on the presence of crystallinity of the samples. Amorphous polymers exhibit only decomposition at elevated temperatures. The semicrystalline samples, however, show a distinct melting endotherm prior to decomposition. Specifically, samples below 19% tacticity only decompose, whereas at or above 23% isotactic content, melting is observed. As discussed elsewhere, the melting point of a polymer is dependent upon the mean length of the isotactic placement, μ .^{14,20} The higher the value of μ , the less is the probability of change from isotactic triad to heterotriad and the longer is the isotactic sequence. Thus, with an increase in μ , there is less disruption in the isotactic sequence, and thus higher melting point crystallites should result. A comparison of samples of the same tacticity but varying μ exemplifies this point. For example, both PDMA/28/1.28 and PDMA/28/5.33 have 28% tacticity; but since the latter has a higher value of μ (10.3 and 15), its melting point is also 14°C higher (309 and 323°C, respectively).

Not only the thermal properties but also the morphologic, optic, and mechanical properties of this series of polymer undergo a drastic variation between 19 and 23% isotactic content. This apparently is a crucial range, because above this level of tacticity the behavior is that of a semicrystalline material and below this level the polymer is amorphous.

Crystallinity and Morphology

The variation of properties of these polymers with change of tacticity is closely associated with the change in crystallinity and morphology. The polymers are amorphous at and below 19% isotactic content. At 23% tacticity, the polymer is partially crystalline and above this value, the level of the crystallinity is increased with an increase in percent tacticity.* The x-ray diffraction patterns of samples at 19% tacticity (Fig. 2) shows only a diffuse halo due to amorphous

* It is important to point out that under the same conditions of sample preparations (solution casting from methylene chloride), no crystallinity was developed for polymers below 19% tacticity. To test whether crystallinity could be induced in these polymers under more favorable conditions, samples of polymers of PDMA-1.9/4.08, 18/3.85, and 14/2.08 which had been cast from the above solvent were annealed further for 3–4 h at 160°C. Even after this treatment, no measurable crystallinity was developed in these samples.

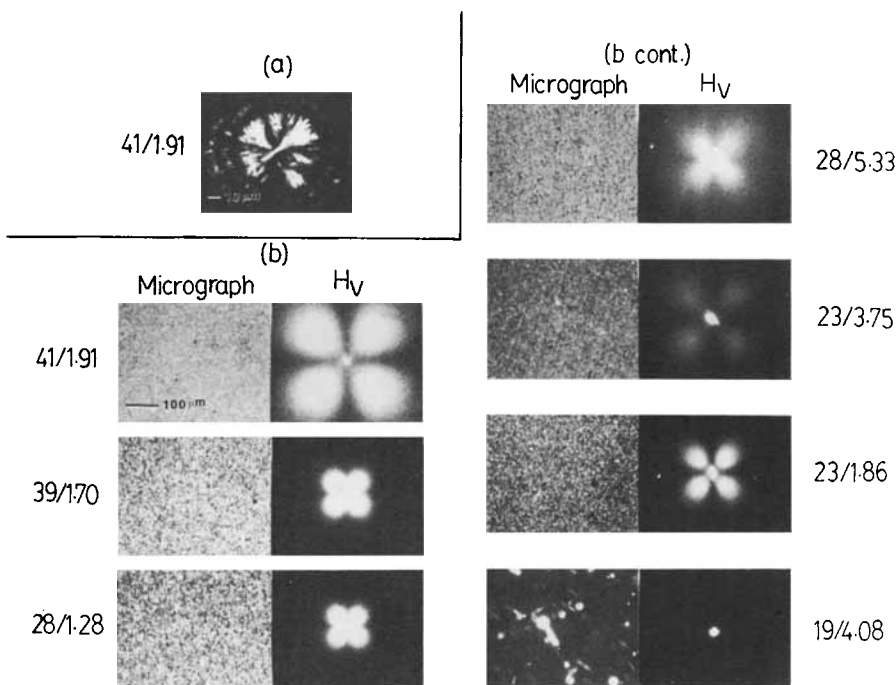


Fig. 3. Photomicrographs of H_V SALS patterns for various PDMA cast films. See text for details.

scattering, whereas at 23% tacticity sharp rings appear which are indicative of the presence of crystallites.[†] The intensity of the rings considerably increased in PDMA/41/1.91. This is anticipated since in other systems, poly(alkyl α -chloracrylates),²¹ for example, an increase in tacticity has been followed by a rapid rise in crystallinity.

Single spherulites of considerable size could be produced upon slow evaporation of solution of PDMA of high tacticity. A well-defined spherulite of PDMA/41/1.91 is shown in Fig. 3(a). To produce this superstructure, the polymer was dissolved in *m*-cresol (20 mg/mL) and evaporated slowly between a microscope slide and a cover slip. Since the morphology of the films is strongly dependent on the casting condition of the films, we will briefly discuss the morphology of the same films used for sorption and mechanical studies. In Figure 3(b), the optical micrographs and the corresponding H_V light scattering patterns of films of various tacticity are presented. The polymers of tacticity in the range of 23 to 41% are all spherulitic, displaying the typical clover leaf H_V scattering pattern. The spherulites have been directly observed under the scanning electron microscope (see Fig. 4). The polymers of tacticity of 19% and below are isotropic, displaying no optical anisotropic structure within the polarizing microscope. [See Fig. 3(b); the white dots in the polarizing micrograph of PDMA/19/4.08 are caused by dust particles; the same is intentionally overexposed to bring out any possible structure.] A fundamental change in mor-

[†] The authors realize that a very low percentage of crystalline texture is difficult to recognize by WAXS. However, the point here is that a large change in WAXS occurs as tacticity increases from 19 to 23%.

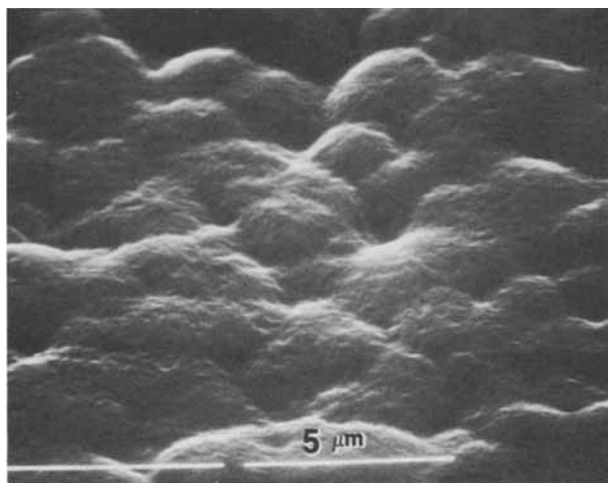


Fig. 4. Scanning electron micrograph of PDMA/41/1/91 cast from methylene chloride.

phology thus has occurred in the tacticity range of 19 to 23% where the crystallinity has developed.

The degree of crystalline domain perfection apparently depends on molecular weight of the polymer as well as on its tacticity. This becomes clear when polymers of the same tacticity but of different molecular weight are compared. For example, although both PDMA/28/1.28 and 28/5.33 have the same tacticity, the former polymer, with a lower molecular weight, forms a more optically anisotropic structure and thus the intensity of the scattered light is two to three orders of magnitude higher. The same is also true when samples 23/3.75 and 23/1.86 are compared. This behavior could be due to the fact that for the polymers of higher molecular weight, a more rapid rise in viscosity during the solidification produces hinderance to molecular molility, as noted elsewhere.²² The polymers of lower molecular weight are thus crystallized more easily, and crystallites are apparently ordered thereby producing anisotropic superstructure which gives rise to the observed H_v light scattering patterns.

Water Sorption

The interest in studying interaction of water with these polymers stems from the following two factors: (a) These polymers absorb different amounts of water, depending on the relative humidity, and the tacticity of the polymer thereby becomes plasticized to a different extent. For practical purposes, it is therefore important to examine the mechanical properties of these polymers, at least at a given humidity level. (b) The gathered data on the interaction with water provide further insight as to the internal structure and morphology of these polymers. In this investigation, these interactions with water were studied in two ways: (1) from the relative amount of water sorbed at equilibrium and (2) from the rate of water sorption.

Equilibrium Water Sorption. The dependence of percent water sorbed at 72% RH on tacticity for various samples is given in Figure 5. An increase in percent tacticity results in a lower water uptake. Part of this phenomenon can

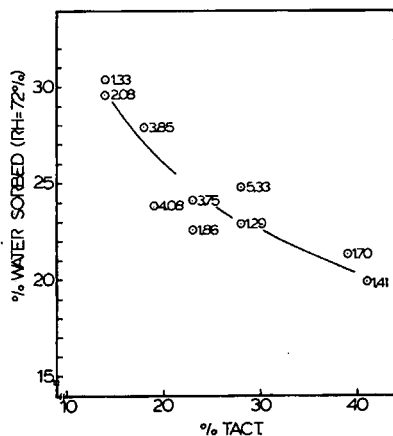


Fig. 5. Effect of tacticity on the percent water sorption for films cast from methylene chloride at a relative humidity of 72%. The values of the intrinsic viscosity are given next to the data point.

be attributed to the increase in the percent crystallinity. However, since the same trend is also observed for the amorphous polymers (compared polymers of tacticity of 19% and lower), it is reasonable to assume that lower uptake of water by the polymers of higher tacticity is related to the difference in the interaction of the water and the various stereoisomers. Whatever the reason, for the difference in hydrophilicity, the polymers of higher water uptake should be plasticized more and therefore be softer.

Rate of Water Sorption. A comparison of the rate of water vapor sorption for the polymer of lowest tacticity (PDMA 14/2.08) to that of highest tacticity (PDMA/41/1.91) at RH of 72% is shown in Figure 6. Generally, an increase in crystallinity is followed by a decrease in the diffusion coefficient of a penetrant, due to inaccessibility of the crystalline regions to the diffusant. However, the apparent diffusion coefficient of water into the highly crystalline polymer PDMA/14/1.91 is higher than that of the amorphous PDMA/14/2.08. The higher

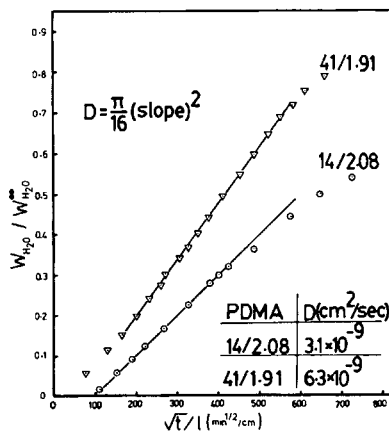


Fig. 6. Comparison of the rate of water sorption of an amorphous PDMA (14/2.08) with that of a semicrystalline PDMA (41/1.91) sample. RH is 74%.

diffusion coefficient of water through semicrystalline PDMA polymers, as compared to that of amorphous PDMA polymers, is often dependent on the morphologic texture. A scanning electromicrograph of the surface of a film of PDMA/41/1.91 was shown earlier in Figure 4. It is noted that there are microvoids present between the spherulites, and it is very possible that the film is porous and channels are present throughout. Such a film is expected to have a higher rate of sorption. The observed sorption behavior is consistent with the data obtained on percent water sorption at equilibrium: the semicrystalline polymers have a higher rate of water sorption due to the presence of these microcapillaries. At equilibrium, however, they retain a lower percentage of water (see Fig. 5) because their amorphous content is lower (provided that, as expected, crystalline regions do not adsorb water as extensively).

Stress-Strain Behavior

The stress-strain measurements were carried out under dry ($RH = 0$, $T = 140^\circ$) and wet ($RH = 72\%$ and ambient temperature) conditions.

Stress-strain of Dry PDMA Above T_g . The mechanical properties of several PDMA polymers at 140°C (about 20°C above their T_g) are shown in Figure 7. The stress-strain behavior shows a *major* difference between the semicrystalline and amorphous samples. At and above 23% tacticity, the mechanical behavior of the samples is that rather typical of semicrystalline polymers displaying a distinct yield point. The modulus and the yield stress are strongly dependent on the tacticity and crystallinity. The samples of higher tacticity show considerable stress hardening which is associated with the orientation as is expected. The polymers of tacticity at or below 19% have behavior expected for amorphous samples. They show no distinct yielding point and are much softer. At this temperature, all these amorphous polymers behaved like an uncured rubber.

Stress-Strain Properties of Samples Under "Wet" Conditions. The

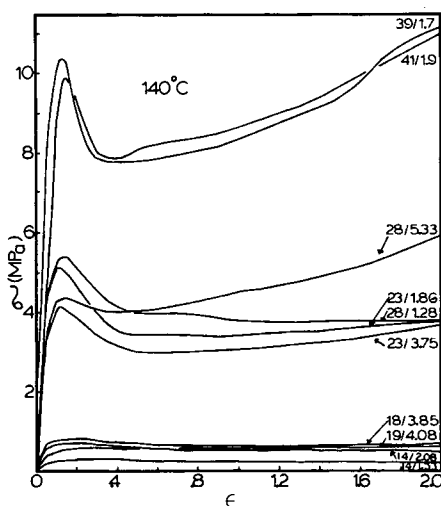


Fig. 7. Stress-strain behavior of PDMA films of different tacticity as measured at 140°C and 0% RH.

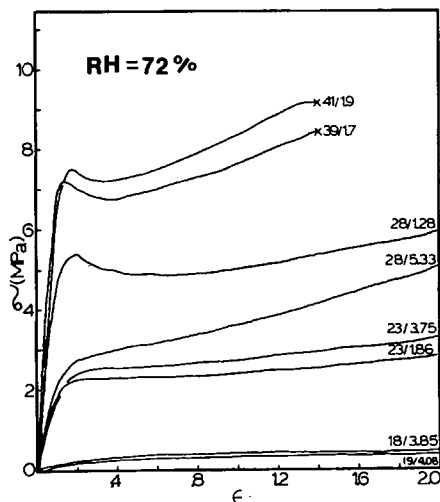


Fig. 8. Stress-strain behavior of PDMA films of different tacticity as measured at relative humidity of 72% and ambient temperature.

stress-strain properties of PDMA in 72% RH and ambient temperature are shown in Figure 8. The highly crystalline samples (tacticity of 39 and 41) still show a definite yield point. But the semicrystalline polymers of lower tacticity become considerably plasticized and lose their yield point. The amorphous polymers, which were lacking crystallites, absorb a considerable amount of water and behave like an uncrosslinked rubber.

Stress-Relaxation

Stress-relaxation measurements at 200% elongation were also carried out under wet and dry conditions. The stress-relaxation of the samples at a RH of 72% and ambient temperature is shown in Figure 9. Under the "wet" condition, the relaxation of amorphous and crystalline samples becomes distinguishably different. All the crystalline samples show a higher rate of relaxation than

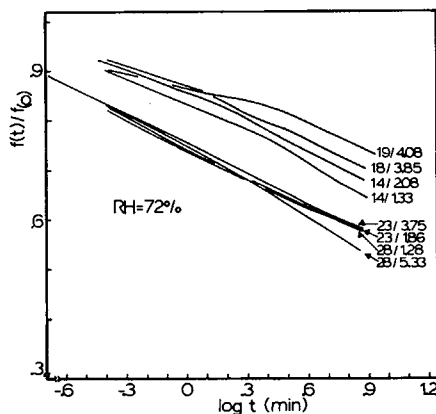


Fig. 9. Stress-relaxation behavior of PDMA films of different tacticity as measured at a relative humidity of 72% and ambient temperature. The fixed elongation is 200%.

amorphous samples. The relaxation of the amorphous samples is also dependent on the molecular weight; thus, between samples 14/1.33, 14/2.08, 18/3.85, and 19/4.08, the rate of relaxation decreases with increase in molecular weight. This phenomenon is presently attributed to the general increase in relaxation time with increase in molecular weight. The stress-relaxation behavior at 140°C (0% RH) is shown in Figure 10. Here again, the rate of relaxation is lowest for amorphous samples and increases with an increase in percent tacticity and thus crystallinity. The enhanced relaxation of partially crystalline polymer, as compared to the amorphous polymers of a comparable molecular weight, can be explained by a higher localized deformation and a greater force experienced by the amorphous chains. If the deformation occurs mainly in amorphous regions, then in the partially crystalline samples higher strain is exerted on the amorphous regions for any given elongation. Thus, although both amorphous and partially crystalline samples were extended 200%, the amorphous regions in the partially crystalline samples experience a higher strain.

Moreover, the stress is also much higher for the crystalline samples (for example, compare the respective stress values at 200% elongation for 41/1.9 and 14/2.08 in Fig. 7). This means that amorphous chains are pulled apart with a much great force in the crystalline polymers. Under these conditions, therefore, the semicrystalline samples relax at a faster rate. Another way of rationalizing the observed phenomenon is to consider the deformation at the molecular level. When an amorphous sample is stretched, the deformation is more or less uniform throughout the sample, with the stress concentration being primarily at the entanglements. On the other hand, when a partially crystalline sample is under strain, the stress is nonuniformly distributed and the tie molecules that are located between the crystallites experience a great deal of force. These chains may relieve their localized tension by various mechanisms, including pulling out of crystallites and/or chemical bond rupture.

In conclusion, because of higher level of stress and due to nonuniformity of deformation and availability of various mechanisms of relaxation, the rate of stress relaxation of the crystalline samples is higher than that of amorphous polymers at 200% elongation.

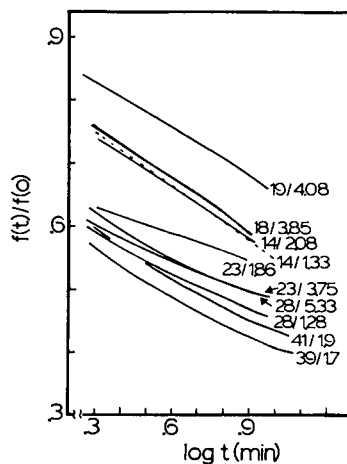


Fig. 10. Stress-relaxation behavior of PDMA films of different tacticity as measured at 140°C and 0% RH. The fixed elongation is 200%.

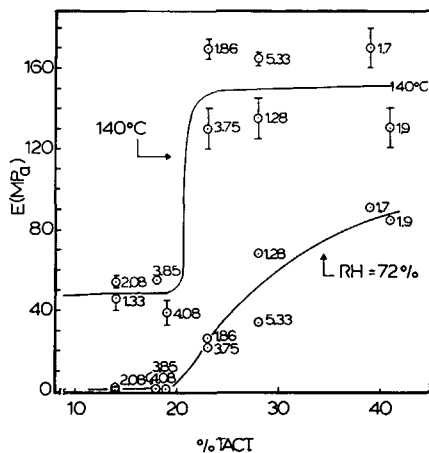


Fig. 11. Effect of change in tacticity on Young's modulus under "dry" (140°C) and "wet" (RH = 72%) conditions. The values of the intrinsic viscosity are given next to the data points.

CONCLUSIONS

A summary of the dependence of the modulus of the PDMA samples on tacticity at both dry and wet conditions is shown in Figure 11. At a relative humidity of 72% and ambient temperature, all the amorphous samples absorb enough water to be totally plasticized to a rubbery state ($E = 0.5$ to 1.0 MPa for a lightly crosslinked rubber). At and above 23% tacticity, the relative amount of sorbed water is lower than that of amorphous polymers. Moreover, they are crystalline and therefore their modulus is higher. The increase in modulus with percent tacticity is smoother and less pronounced relative to the dry state due to the increased plasticization effects caused by the sorbed water. At 140°C, the modulus of the amorphous samples (around 50 MPa) is higher than that of a typical rubber. This is because these polymers are only about 20°C above T_g and are actually in the transition (leathery) region. An increase in tacticity from 19 to 23% results in a threefold rise (from 50 to 150 MPa) in the modulus of the polymer. This is, of course, attributed to the change of morphology of the polymer from amorphous to the semicrystalline state. Above 23% tacticity, the polymers are all semicrystalline and behave accordingly.

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