Equations of State and Predictions of Miscibility for Hydrocarbon Polymers

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ABSTRACT: The pressure–volume–temperature properties of a number of hydrocarbon polymers, including a series of ethylene–propylene copolymers, have been measured. These data, in the melt state, have been fit to equations of state. The characteristic parameters from the equations of state are related to thermodynamic properties of the polymers and have been correlated with their structure. The pure component data have been used to make predictions about the miscibility of the polymers with each other. It was found that, even in these nonpolar materials the enthalpy of mixing should dominate the behavior. The ethylene–propylene copolymers are predicted to be miscible for less than 15% differences in monomer contents at molecular weights of 10^5.

Introduction

Many equations of state have been suggested to describe the liquid state of polymers. Simple lattice theories are not adequate in describing their behavior, and as a result various other theories have been developed which allow for the possibility of volume changes. Generally, they are derived by introducing a free volume term into the partition function. The most widely used equations of state for polymer liquids are the theory ascribed to Flory, Orwoll, and Vrij (FOV),[1,2] the lattice fluid theory of Sanchez and Lacombe,[3] the Simha and Somcynsky equation,[4] which is similar to the equation derived previously by Henderson,[5] and a cell model recently applied by Dee and Walsh[6] which comes from the work of Lennard-Jones and Devonshire[7] and Prigogine and co-workers[8] (LDP). These equations of state differ in the treatment of the free volume term and the energy term in the partition function. Discussions of the relative performance of these equations in describing pressure–volume–temperature (PVT) data have been presented.[6,9] They provide us with valuable thermodynamic information in that the characteristic parameters in the equations are related to various thermodynamic properties of each polymer. They also can be used to make predictions concerning the thermodynamic properties of mixtures.

A necessary but not sufficient criterion for miscibility to occur is that the free energy of mixing be negative. A precise requirement is that its second differential with respect to composition be positive over the entire composition range. The free energy of mixing can be considered as arising from three contributions, the combinatorial entropy, an interactional term that is usually specified by an interaction parameter, and a contribution from free volume changes on mixing. The last of these is often included within the interaction term, but this is not satisfactory for a realistic description of polymer mixtures. The free volume contribution is in principle predictable from the equation of state and is expected to be unfavorable for mixing.

The combinatorial entropy is favorable for mixing. It depends on the number of molecules present and is therefore very small for the case of mixtures of high polymers. For miscibility to occur, it is therefore necessary that the interaction term be favorable, or if unfavorable very small. A favorable interaction can occur as a result of specific attractive interactions between polymers or specific repulsive interactions between segments on the same polymer and has been the subject of much discourse.[10] It is by nature a complicated phenomenon and difficult to describe quantitatively in a physically realistic way. Much simpler are the nonpolar dispersive interactions which are normally expected to give unfavorable interactions. The pure component properties described by the equation of state can in principle be used to predict the size of these interactions. If these are very small, a small unfavorable interaction parameter will result and miscibility can occur. Such systems have been studied for example in the case of mixtures of deuterated and nondeuterated samples of the same polymer,[11] and in the case of mixtures of simple hydrocarbon polymers.[12]

In this paper we report pressure–volume–temperature data for various hydrocarbon polymers and fit them to equation of state models for the polymers. We then use this information to make predictions about the expected miscibility of the polymers with each other.

Theory

There are numerous equations of state in the literature which are proposed to describe polymer liquids. In this paper, we mainly use two equations of state: the FOV model[1,2] and the LDP model.[6] The FOV equation has been most extensively applied; the LDP equation is equally easy to apply and has been found to give a much better fit to PVT data.[6] We examine the molecular structure

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dependence of the characteristic parameters in these two equations.

The equation of state of Flory and co-workers is given by

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/(\tilde{T}\tilde{v}) \qquad (1)$$

where $\tilde{P}$, $\tilde{v}$, and $\tilde{T}$ are reduced variables defined as

$$\tilde{P} = P/P^* \qquad \tilde{v} = v/v^* \qquad \tilde{T} = T/T^* \qquad (2)$$

P, v, and T being the actual pressure, volume, and temperature and P^*, v^*, and T^* the characteristic parameters (hard-core reduction parameters) which must be found in order to characterize the system. The characteristic pressure and temperature are given by

$$P^* = \epsilon^*/v^* \qquad T^* = \epsilon^*/(ck) \qquad (3)$$

where ϵ^* is the mean intermolecular energy per contact pair, $3c$ is the number of external degrees of freedom per mer, and k is the Boltzmann constant.

The LDP model differs from the FOV model in that the latter uses a van der Waals potential to describe the attractive interaction between the mers in the system. The LDP model employs a Lennard-Jones 6–12 potential to describe this interaction. The LDP equation of state is given by

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{1}{(1 - \gamma^{1/3}\tilde{v}^{-1/3})} - \frac{2}{\tilde{T}}\left(\frac{A}{\tilde{v}^2} - \frac{B}{\tilde{v}^4}\right) \qquad (4)$$

where the definitions of $\tilde{P}$, $\tilde{v}$, and $\tilde{T}$ are the same as those for FOV. The values of γ, A, and B depend on the fraction of the cell volume filled at closest contact and factors taking into account interactions with other than the nearest neighbors, and these depend on the specific cell geometry used. We use a hexagonal close-packed geometry, for which $\gamma = 0.8909$, $A = 1.2045$, and $B = 1.011$. The goodness of fit is not found to be very sensitive to the geometry used, though the values of the reduced parameters will be different.

When applying these equations to mixtures, we use the following rules: (a) The hard-core mer volumes, V^*, are defined to be equal:

$$V^*_1 = V^*_2 = V^* \qquad (5)$$

(b) The hard-core volume of the mixture, v^*, is equal to the sum of the hard-core volumes of the components:

$$v^* = \sum r_i N_i V^* \qquad (6)$$

where N_i is the number of molecules of component i having r_i segments. (c) The hard-core pressure and temperature of the mixture are given by

$$P^* = \phi_1 P^*_1 + \phi_2 P^*_2 - X_{12}\phi_1\theta_2 \qquad (7)$$

and

$$T^* = \frac{P^*}{\phi_1 P^*_1/T^*_1 + \phi_2 P^*_2/T^*_2} \qquad (8)$$

where ϕ_i is the hard-core volume fraction of component i, θ is a site fraction (which is equal to a volume fraction if the areas per unit volume are assumed equal), and X_{12} is an adjustable interaction parameter which describes the interchange energy of the mixture.

We can then compute the chemical potential using the expression

$$\Delta\mu_1 = kT\left[\ln\phi_1 + \phi_2\left(1 - \frac{r_1}{r_2}\right)\right] + r_1\epsilon^*_1\left[3\tilde{T}\ln\left(\frac{\tilde{v}_1^{1/3} - \gamma}{\tilde{v}^{1/3} - \gamma}\right) + \tilde{P}_1(\tilde{v} - \tilde{v}_1)\right] + F(\tilde{v}) \qquad (9)$$

where

$$F(\tilde{v}) = r_1\epsilon^*_1\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + \frac{r_1 v^*}{\tilde{v}} X_{12}\theta_2^{\,2} \qquad (10)$$

for the FOV equation and

$$F(\tilde{v}) = r_1\epsilon^*_1\left[A\left(\frac{1}{\tilde{v}_1^{\,2}} - \frac{1}{\tilde{v}^2}\right) - \frac{B}{2}\left(\frac{1}{\tilde{v}_1^{\,4}} - \frac{1}{\tilde{v}^4}\right)\right] + r_1 v^* X_{12}\theta_2^{\,2}\left(\frac{A}{\tilde{v}^2} - \frac{B}{2\tilde{v}^4}\right) \qquad (11)$$

for the LDP model.[13] For the FOV model $\gamma = 1$ and for the LDP model $\gamma = 0.8909$. ϵ^* is defined by eq 3.

Using eqs 9–11 and a similar expression for $\Delta\mu_2$, we can compute $\Delta\mu_1$ and $\Delta\mu_2$ and locate the phase diagram for this binary system by seeking solutions to the equation

$$\Delta\mu_1^{\,\mathrm{I}} = \Delta\mu_1^{\,\mathrm{II}} \qquad (12a)$$

$$\Delta\mu_2^{\,\mathrm{I}} = \Delta\mu_2^{\,\mathrm{II}} \qquad (12b)$$

where the superscripts I and II indicate two different phases. These solutions, if they exist, are determined numerically.

The spinodals are determined by finding solutions of the equation

$$\left.\frac{\mathrm{d}\Delta\mu_1}{\mathrm{d}\phi_2}\right|_{\phi_2^{\mathrm{s}}} = \left.\frac{\mathrm{d}\Delta\mu_2}{\mathrm{d}\phi_2}\right|_{\phi_2^{\mathrm{s}}} = 0 \qquad (13)$$

where ϕ_2^{s} denotes the value of ϕ_2 at which eq 13 is satisfied. These values are determined numerically for each equation of state.

In the simplest possible case the interaction parameter is given by

$$X_{12} = P^*_1 + P^*_2 - 2(P^*_1 P^*_2)^{1/2} \qquad (14)$$

This geometric mean equation is equivalent to the approach used in the solubility parameter theory where the heat of mixing is proportional to the square of the difference in solubility parameters. This is a relatively crude approximation but is most likely to be applicable to nonpolar mixtures such as the ones considered here.

Experimental Section

Materials. The PVT properties of polymers depend only on the local molecular structure and are a simple average over the entire sample. For this reason they are not dependent on molecular weight for number averages over 5000 within experimental error.[14] Likewise they are not expected to depend on small quantities of impurities and additives in most cases. Samples of the same polymer from different sources are therefore expected to give essentially the same results.

The high-density polyethylene and polypropylene were commercial samples. The poly(ethylene-*co*-propylene) samples at 16 and 24, 43, and 77% (wt) ethylene were prepared in a Ziegler polymerization using a vanadium-based catalyst in hexane solution, and are essentially random copolymers with most-probable molecular weight distributions. The atactic polypro-

Table I
Properties of Polymers

	M_w	M_w/M_n
high-density polyethylene	126 000[a]	4.5[a]
polypropylene	301 000[e]	4.46[e]
atactic polypropylene	53 400[d]	11.5[a]
poly(1-butene)	316 000[b] 185 000[c]	2.4[b]
atactic poly(1-butene) (hydrogenated poly(vinyl ethylene))	95 000[d]	<1.1[a]
polyisobutylene	597 000[b] 400 000[c]	1.8[b]
polybutadiene	233 000[c]	1.67[c]
hydrogenated polyisoprene (alternating ethylene–propylene 40% (wt))	170 000[d]	<1.1[a]
poly(ethylene-*co*-propylene) (EPR)		
16% (wt) ethylene	75 000[d]	2.1[a]
24% (wt) ethylene	84 400[d]	2.1[a]
43% (wt) ethylene	134 000[d]	2.6[a]
77% (wt) ethylene	160 000[d]	3.0[a]

[a] GPC relative to polyethylene standards. [b] GPC relative to polystyrene standards. [c] Manufacturers quotation. [d] Light scattering. [e] GPC with polystyrene standards: universal with $K = 0.000\ 137$, $\alpha = 0.75$.

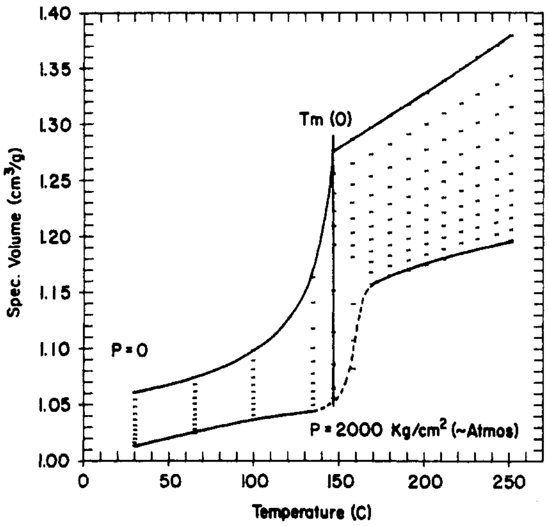

Figure 1. PVT data for high-density polyethylene with lines drawn through the data at 0 (extrapolated value) and 2000 kg/cm². The data are shown for every 200 kg/cm² though this is only half the actual data for clarity. An estimate of the zero pressure point of complete melting is also shown.

Table II
Reduction Parameters

polymer	P^* (J/cm³)	v^* (cm³/g)	T^* (K)	s^2 (MPa²)
FOV Equation of State				
polyethylene[a]	472	1.0047	6812	10
polypropylene	408	1.0083	6802	11
atactic polypropylene	412	0.9983	6740	13
hydrogenated polyisoprene	444	1.0031	6896	9
EPR 16% ethylene	442	0.9970	6719	12
EPR 24% ethylene	437	1.0001	6757	12
EPR 43% ethylene[c]	448	0.9988	6788	12
EPR 77% ethylene[b]	465	1.0095	6816	12
poly(1-butene)	372	1.0035	7034	12
hydrogenated poly(vinylethylene)	396	0.9832	7043	10
polyisobutylene[b]	441	0.9594	7780	10
polybutadiene[b]	497	0.9643	6825	15
LDP Equation of State				
polyethylene[a]	550	1.1245	4393	2
polypropylene	461	1.1381	4484	2
atactic polypropylene	476	1.1277	4495	2
hydrogenated polyisoprene	526	1.1271	4528	3
EPR 16% ethylene	498	1.1270	4468	2
EPR 24% ethylene	502	1.1275	4460	2
EPR 43% ethylene[c]	518	1.1263	4460	2
EPR 77% ethylene[b]	534	1.1361	4463	2
poly(1-butene)	460	1.1331	4781	3
hydrogenated poly(vinylethylene)	488	1.1075	4732	4
polyisobutylene[b]	576	1.0735	5160	4
polybutadiene[b]	540	1.0733	4665	4

[a] Average of five high-density polyethylene runs. [b] Average of two runs. [c] Average of three runs.

pylene was prepared in a similar way. The isotactic poly(1-butene) and polyisobutylene samples were obtained from Scientific Polymer Products. The polybutadiene was a standard material from Polysciences and was made by anionic polymerization. The atactic poly(1-butene) was made by hydrogenation of poly(1,2-butadiene), and the hydrogenated polyisoprene was made from poly(1,4-isoprene). Both materials have the narrow molecular weight distribution that typifies organolithium-initiated anionic polymerization. The characterization data of the polymers are presented in Table I.

PVT Measurements. Densities of the polymers were measured at 25 °C and atmospheric pressure using an autopycnometer (Micromeritics). The changes in density as a function of temperature and pressure were measured using an apparatus that has been fully described elsewhere.[15] For solid samples, it consists of a sample cell containing about 1–1.5 g of sample and mercury as a confining fluid. A flexible bellows closes off one end of the cell. The movement of the bellows on changing temperature or pressure is used to calculate the volume change of the sample cell. In the isothermal mode, volume readings are obtained at fixed pressure intervals (usually 10 MPa) at a constant temperature. After measurements along an isotherm, the temperature is increased by 8–10 °C and the process is repeated. The absolute accuracy of the device is of the order of 10^{-3} cm³ g⁻¹; however, volume changes as small as 10^{-4} cm³ g⁻¹ can be resolved. A version of the PVT apparatus is available as a complete instrument from Gnomix Research, Boulder, CO. An example of the data for polyethylene is given in Figure 1.

Results

Blocks of PVT data were fit to the two equations of state. For most of the polymers, blocks were chosen from 150 to 250 °C and from 10 to 200 MPa and typically contained about 200 data points. For an ethylene–propylene copolymer the volume increases smoothly with temperature and decreases with pressure over this region. In the case of polyethylene as shown in Figure 1 it was necessary to remove a few of the low-temperature high-pressure data points within this block due to pressure-induced crystallinity. Likewise for the polypropylene it was necessary to start the data at 160 °C due to crystallinity. All other polymer data blocks were simple.

We performed a nonlinear least-squares fit of each equation by minimizing the regression sum of squares:

$$s^2 = \sum_i (P_{i,\mathrm{data}} - P_{i,\mathrm{fit}})^2/(N-3) \qquad (15)$$

where N is the number of data points, P_{data} is the measured pressure at a given value of (V,T), and P_{fit} is the value of the pressure predicted by the equation. Examples of the results of this fitting procedure have been presented in the literature.[14,16] Table II summarizes the results for the values of P^*, v^*, T^*, and s^2 obtained in this way for the two equations of state for the homopolymers. The errors by repeat measurement are about ±20 J/cm³ in P^* and ±100 K in T^*. A value of s^2 around 0.2 MPa² represents the precision of the data and is obtained for very small blocks of data. Since the equations do not provide a perfect fit, the values of the reduction parameters will vary if one looks at blocks of data from different regions, and this effect will be much worse with the FOV equation since

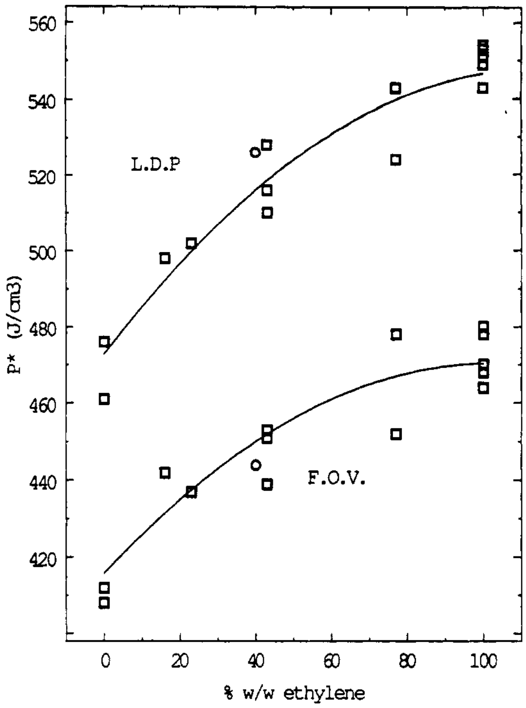

Figure 2. P^* values from the FOV and LDP equations of state for (squares) ethylene–propylene copolymers plus polyethylene and polypropylene; (circles) a hydrogenated polyisoprene, strictly alternating ethylene–propylene copolymer. The lines are second-order fits to the data.

this provides a worse fit to the data. Of all the parameters P^* is most sensitive to the data, being susceptible to small systematic errors. Thus, one must be careful how one uses this if the data are obtained from different sources. Variations as high as 10% may occur if one just takes literature data of different accuracy from different sources. When making comparisons, it is best to take equivalent data blocks obtained in the same way from the same apparatus.

The results for the ethylene–propylene copolymers are plotted as a function of composition in Figures 2 and 3. The v^* values range from 0.997 to 1.009 cm^3/g (FOV) and from 1.123 to 1.138 cm^3/g (LDP) and show no systematic trend. Since these values contain the error in the starting density as well as in the fitting, the differences are considered to be within experimental error. Also shown is a hydrogenated polyisoprene which is in effect an alternating copolymer. This shows no difference from the random copolymers within experimental error. We have also obtained data for many commerical terpolymers, not presented here, which contain on the order of 5% of another monomer. For the reasons discussed above and since the third monomers are also simple hydrocarbons and therefore not very different in chemistry from polyethylene and polypropylene repeat units, these data fit well onto the same graph though there may be small systematic deviations.

The relative values of the parameters are very much as one would expect. The P^* values scale with the cohesive energy density. Those least polar polymers with the most CH_3 groups are generally lowest while the unsaturated hydrocarbon polymer, polybutadiene, is highest. The T^* values scale with the energy divided by the entropy (or degrees of freedom per mer). These are all very similar except for the polyisobutylene which is substantially higher. It is tempting to relate this to some of the other abnormal properties of polyisobutylene. The high T^* theoretically comes from a low value for the number of external degrees of freedom per mer. A high T^* arises in the fit due to a low value of the expansion coefficient which in turn is consistent with a low free volume. Polyisobutylene also has the lowest core volume of all saturated hydrocarbons. One can also note that the data for isotactic poly(1-butene) is close to that of hydrogenated poly(vinylethylene) which is in effect an atactic version of the former, and that tactic and atactic polypropylene are very similar. This result parallels the finding from neutron scattering that isotactic and atactic polypropylene are miscible in the melt state.[17] It is apparent that the PVT properties of the melt are not much affected by tacticity.

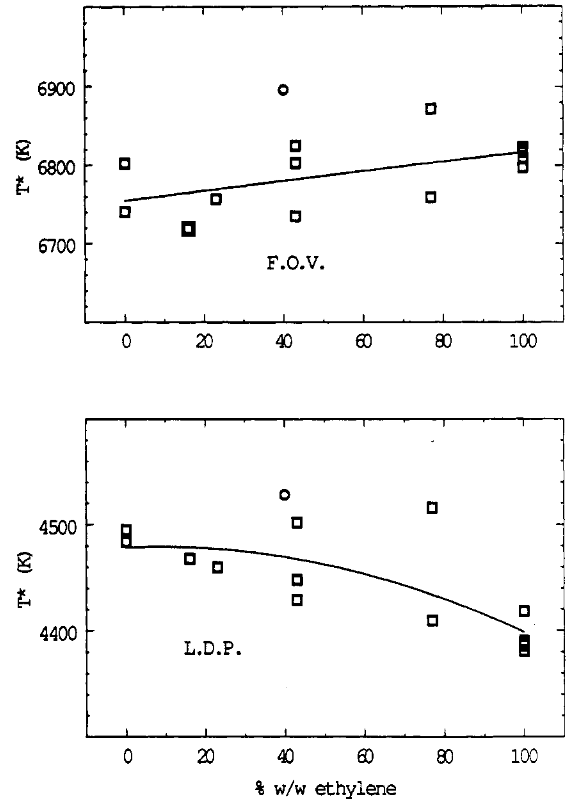

Figure 3. T^* values from the FOV and LDP equations of state for (squares) ethylene–propylene copolymers plus polyethylene and polypropylene; (circles) a hydrogenated polyisoprene, strictly alternating ethylene–propylene copolymer. The lines are second-order fits to the data.

One can estimate the miscibility of two polymers using the equations outlined above. Comparable calculations, but expressed in terms of expansion coefficient and thermal pressure coefficient, have been presented in the literature.[18] For two polymers of 10^5 molecular weight having T^* values of 6900 K (FOV) and P^* values of about 450 J/cm^3, a difference of 10 J/cm^3 in P^* is sufficient to give immiscibility with a critical temperature (UCST) near room temperature. One should note that this conclusion relies on the geometric mean approximation of eq 14. A difference in T^* values of 250 K is sufficient to give immiscibility with a critical temperature (LCST) near room temperature. A difference of about 8 J/cm^3 in P^* and 190 K in T^* is sufficient to give both LCST and UCST behavior. The LDP model will give the same effects with about the same percentage differences in P^* and T^*. These differences are unfortunately of the order of the uncertainty in the parameters, especially in the case of P^*. As any of these differences increase beyond this, the system very quickly approaches complete immiscibility over the entire accessible temperature region. Lower molecular weight polymers will tolerate bigger differences in the parameters, but a reduction in molecular weight by a factor of 4 would only increase the differences allowed by a factor of approximately 2.

It is obvious from examining the parameters that, despite the fact that these are all nonpolar polymers, it is the differences in P^* which will most cause immiscibility. Two polymers in the list, poly(1-butene) and polypropylene, have been reported to be miscible,[19] although other evidence suggests this may not be the case.[20] They do not have dissimilar parameters, and one might have predicted that they were borderline miscible. Our errors are however too large to accurately predict the result in any single case. These random errors are those arising from repeat measurements on identical samples. While errors in the density are not large with our equipment, the state parameters depend on derivatives where the errors are more pronounced. Ideally one would want a significant improvement in accuracy of measurement if one were to use the data for such predictions. A series of experiments done on a set of copolymers, as in the following example, also reduce our level of uncertainty to some extent.

The data for ethylene–propylene copolymers in Figure 2 led us to believe that a 15–20 wt % difference in ethylene content would be tolerated for miscibility at $M \approx 10^5$. One might expect a straight line relationship for P^* with ethylene content, but it appears to be a little curved, just within experimental error. If this is so, it would suggest a greater toleration of compositional differences with higher ethylene content. These predictions have yet to be born out by experimental studies, but if found to be correct, they would appear to be somewhat at odds with suggestions that polyethylenes with small differences in branching are immiscible,[21] although this would depend on how the properties are related to branch length.

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Registry No. Polyethylene (homopolymer), 9002-88-4; ethylene/propylene (copolymer), 9010-79-1; polypropylene (homopolymer), 9003-07-0.