Solubility of Polystyrene in Certain Vegetable Oils, Essential Oils and Their Constituents

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ABSTRACT

Certain food items have been shown to be incompatible with the expanded polystyrene used for the manufacture of food containers. Using ^{14}C polystyrene (synthesized in such a way as to approximate the structure of commercial polystyrene), it was determined that this incompatibility was due, in part, to the dissolution of polystyrene by certain essential oils. Citronella, limonene and terpinene (constituents of many flavor oils) were found to be excellent solvents for polystyrene, solubilizing almost half a gram per gram of solvent at room temperature.

INTRODUCTION

EXPANDED POLYSTYRENE is used extensively for protecting, storing and serving many different food products.

A letter appearing in the New England Journal of Medicine (Phillips, 1979) inferred, with scanty experimental qualifications, that polystyrene was being solubilized by lemon-flavored tea and anyone who drank this mixture from a polystyrene container "will also consume an appreciable amount of the container itself in solubilized form." In the same paragraph Phillips mentions that "polystyrene is carcinogenic in laboratory animals (Oppenheimer et al., 1955)." The controversy surrounding this letter (Bishop, 1980) culminated in the release, by the National Cancer Institute, of laboratory reports tentatively clearing the styrene monomer and beta-nitrostyrene of any cancer-causing activity (National Cancer Institute, 1979). The plastics industry cried victory (Anonymous, 1980), but questions were raised by the incident concerning the potential of food contamination by styrene polymer, questions that had no real answers in the literature.

Much is known about the toxicity of styrene (Harkonen, 1978; Leibmen, 1975) and carefully documented results have been reported on the migration of this substance from polystyrene packaging material into foods (Pfab and Mucke, 1977; Davies and Dunn, 1973). Boundy and Boyer (1952), in their outstanding treatise on styrene and styrene polymer, mention incompatibilities between certain aromatic oils and polystyrene, including the softening and weakening effects of these solvents. However, the question of solubilities and or migration of polymers of styrene into foods was not, nor has since been, addressed.

The current study investigated the solubility of polystyrene in certain vegetable and essential oils and explored several methods to determine its solubility.

EXPERIMENTAL

Synthesis of ^{14}C Polystyrene

A sealed glass ampule containing 105 mg of styrene (ring-^{14}C) with a specific activity of 0.246m Ci/m mole (Lot No. 1193-162 New England Nuclear) in a nitrogen atmosphere was submerged in a heated oil bath at 110°C for 144 hr, after which the temperature was raised to 120°C for an additional 10 hr of polymerization. Small quantities of styrene which have been polymerized in this manner often contain residual styrene and very low molecular weight polymers which are not present in commercial grades of expandable polystyrene (Boundy and Boyer, 1952). To remove these possible contaminants, the polystyrene as described above was dissolved in 7.5 ml of methyl ethyl ketone (Reagent grade). To this solution 5 ml of 100% ethanol were added slowly with constant stirring to precipitate the polystyrene. Centrifugation in a corex tube at 4000 G for 20 min produced good separation of the precipitant. The supernatant was discarded and the pellet was washed with 10 ml of ethanol, removed and allowed to dry in a draft of warm air at 60°C. The procedure was repeated with the pellet being dissolved in 10 ml of methyl ethyl ketone and precipitated with 3 ml of ethyl alcohol. Several 5 μl aliquots of the supernate was removed after centrifugation and each was dissolved in 10 ml of Aquasol scintillation cocktail. Its activity was then determined against a quenched carbon-14 liquid scintillation standard curve (methyl ethyl ketone is a good quenching agent) in a Beckman LS 100C liquid scintillation system. The activity of the solution indicated more than 2% of the specific activity of the styrene remained in the supernatant; therefore, additional purification was necessary to rid the polystyrene of low molecular weight moieties. The purification procedure was repeated several more times using 10 ml of methyl ethyl ketone and 4 ml of ethanol for precipitation until the activity of the supernatant came within 20% of background.

After drying to a constant weight, an aliquot of the purified polystyrene was subjected to gel permeation chromatography. All chromatography was performed on a Waters Associates Model 244 gel permeation chromatograph with uninhibited tetrahydrofuran (THF) as a solvent at a flow rate of 2 ml/min. Solutions of the samples in THF were injected using the Model U6K Injector which was connected, for the duration of the run, to a micro styrogel column system with the following exclusion limits: 10^6, 10^5, 10^4, 10^3, 500 A°. The entire system was operated at ambient temperature with a Model 401 Differential Refractometer detector and Model 440 UV Absorbance Detector at 254 nanometers and 2 absorbance units full scale. The Waters Model 730 Data Module with GPC option was utilized for plotting the chromatograms and to perform integration parameters. Two samples of commercial expandable polystyrene were compared with the ^{14}C polystyrene (Fig. 1). Subjective evaluation of the molecular weight distributions demonstrated relative equivalaency, at least for the purpose of this series of experiments.

Preparation of ^{14}C polystyrene for solubility study

The activity of the ^{14}C polystyrene was sufficiently high to allow for dilution with cold commercial polystyrene.

Commercial polystyrene in pre-expanded form was procured from a local manufacturer of plastic foam cups. The polystyrene in this pre-expanded form had a density of about 100 mg per cubic centimeter (much denser than the final expanded form) and were spherically shaped with a diameter between 0.5–1.0 millimeter. This form was much easier to work with than the fully expanded polystyrene. Ten grams of this material were dissolved in 100 ml of methyl ethyl ketone, with a subsequent addition of 5 ml of methyl ethyl ketone, in which had been dissolved 42 mg of the purified ^{14}C polystyrene from above. The solution was thoroughly mixed and divided as 10 ml aliquots into corex centrifuge tubes which contained 5 ml of 100% ethanol. The contents of the tubes were stirred vigorously with glass stirring rods and subjected to 4000 G for 20 min. The supernate was discarded and the pellet washed several times with 100% ethanol. The pellets were combined and kneaded together into a viscous plastic mass. This mass was carefully rolled into a long thin cylinder about 1–2 mm in diameter and cut, while still in plastic form, with a sharp, disposable scalpel, into small beads with weights of 10–50 mg. These were then placed in a drying

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oven (60°C) until their weight stabilized (48 hr). They were thoroughly washed in 100% ethanol, washed a second time in deionized water, then rinsed over a fine stainless steel screen to assure the removal of any fine particulate matter. After drying, the beads were ready for use in the solubility test, with an estimated specific activity of approximately 10 microcuries per gram.

Choice of vegetable oils, essential oils and aromatics

All oils and aromatics used in this study were food grade and procured from appropriate purveyors. The rancid corn oil was produced by heating corn oil for 2 hr at 177°C (350°F) with constant exposure to air. The constituents of flavor oils were chosen from compounds suggested by Guenther (1950) as being present in citrus and other related aromatic oils. All were provided by the Sigma Chemical Company.

Observational method

The pre-expanded beads of commercial cup grade polystyrene

Table 1—Polystyrene solubility (mg/g)

	^{14}C Labeled polystyrene (Synthesized)			Commercial pre-expanded beads	
	20°C 1 hr	20°C 24 hr	20°C 7 days	20°C	75°C
Food vegetable oils:					
Almond oil (sweet)	0.001	0.003	0.006	–	–
Corn oil	0.002	0.002	0.002	0	0
Corn oil (Peroxide Value 130)	0.015	0.017	0.018	0	0
Olive oil	0.001	0.005	0.020	–	–
Peanut oil	0.001	0.006	0.007	–	–
Safflower oil	0.003	0.007	0.007	–	–
Sunflower oil	0.001	0.001	0.001	–	–
Soy oil	0.002	0.005	0.009	–	–
Linoleic acid	0.002	0.002	0.002	0	0
Essential oils:					
Almond oil (bitter)	10.70	12.50	124.01	–	–
Clove oil	1.80	82.30	211.10	166	257
Eucalyptus oil	6.90	213.60	460.20	337	497
Lemongrass oil	11.30	116.70	289.10	262	920
Lemon oils:					
Fivefold[a]	9.00	143.10	386.60	315	425
Fivefold[b]	10.70	86.20	194.70	186	252
Distilled[b]	20.60	187.20	347.10	318	476
U.S. Extra[a]	12.90	164.70	299.10	283	393
Terpeneless[a]	7.20	155.50	236.60	201	351
Oil phase essence[b]	22.00	173.80	294.20	276	404
Terpenes, blended[b]	15.60	254.30	496.30	401	423
Terpenes, Fivefold[a]	15.60	288.20	577.60	413	539
Lemon essence water phase[b]	0	0	0	0	0
Essential oil constituents:					
Citral	12.70	14.60	37.50	33	566
Citronellal	8.70	212.70	523.00	402	594
Decyl Aldehyde	5.78	12.34	96.67	84	426
Geraniol	0.01	0.02	0.11	0	240
Limonene-D	15.30	287.40	415.10	313	406
Linalool +/–	0.00	0.01	0.03	0	383
Nonyl aldehyde	86.56	256.54	407.22	359	527
Octyl aldehyde	95.06	311.00	487.01	411	664
Terpinene	12.40	269.30	412.00	370	511
Water	0	0	0	0	0

[a] Citrus and Allied Essences Limited 65 S. Tyson Ave. Floral Park, NY
[b] Sunkist Growers Inc. Corona, CA 91720

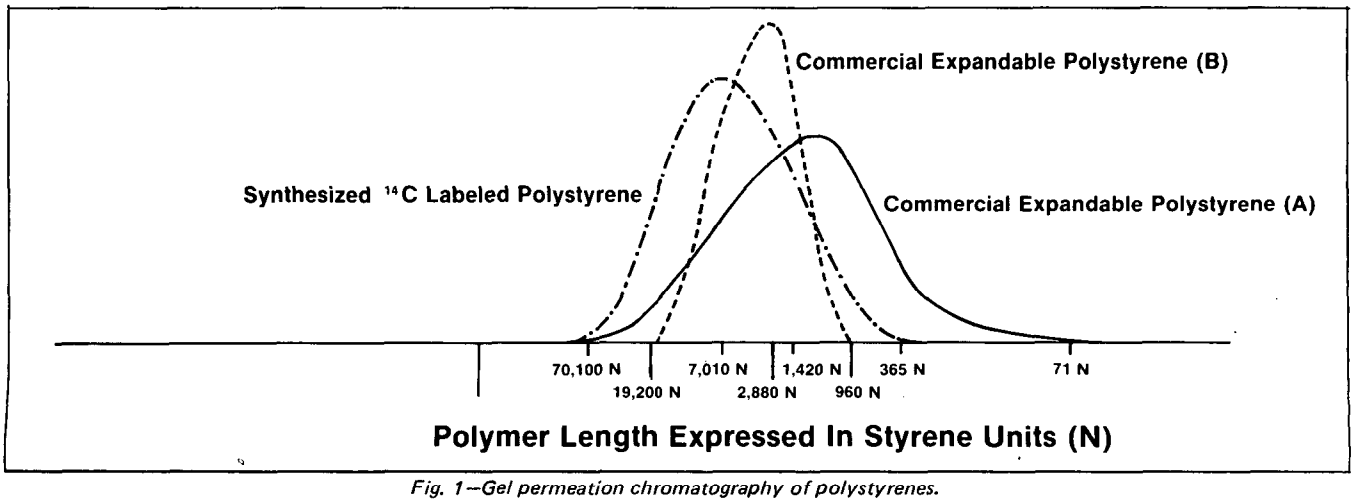

Fig. 1—Gel permeation chromatography of polystyrenes.

mentioned above were ideal for solubility determinations. One gram of the potential solvent was placed in a capped vial which also contained a Teflon-coated magnetic stir bar. The temperature was stabilized and a few beads of pre-expanded polystyrene were added with moderate agitation. If the beads dissolved, additional polystyrene was added until the solvent seemed saturated. This was duplicated at 20°C and 75°C. The increase in weight of the solvent mixture after all additions of polymer was used to determine solubility.

The same method was used to determine the relationship between solubility and the molecular weight of polystyrene. A polystyrene standard kit, manufactured by the Alfa Division of Ventron Corporation, provided polystyrene standards in the molecular weight range of 2200–600,000.

^{14}C Polystyrene method

After determining the specific activity of the ^{14}C polystyrene-commercial polystyrene mixture, the solubility of this material was determined by the increase in activity of the solvent after exposure to the radioactive polymer.

The polymer beads were placed into vials with the initial weight of bead being proportional to the solubility as determined by the previously described observational method. One gram of food grade oil or aromatic constituent was added to each vial, along with a stir bar. The contents were stirred at a moderate rate to avoid pulverizing the polymer. Centrifugation (2000 G) was necessary to assure complete separation of the oils from the plastic bead remnants and allow for removal of 5-µl aliquots at selected intervals. The aliquots were mixed thoroughly with 10 ml of Aquasol scintillation cocktail in a glass scintillation vial and measured against a quench standard as in the synthesis step above. Samples were removed after 1 hr, 24 hr, and 1 wk. All sampling aliquots were replaced with fresh solvent.

RESULTS & DISCUSSION

MOST of the substances tested showed some capacity as a solvent for polystyrene, Table 1. The exceptions were water and water-soluble essence of lemon flavor.

The vegetable oils all absorbed very small quantities of polystyrene, equivalent to less than 6 mg per gallon of corn oil. The solubility was so slight as to have gone unnoticed by the observational technique. The greater solvency of rancid oil may be due to the presence of aldehydes (Fennema, 1976), several of which proved to be aggressive solvents. (Table 1).

The very high solubility of polystyrene in many of the essential oils tested was unexpected. Reference has been made to these volatile oils as being "weak solvents" or "softeners" of polystyrene (Boundy and Boyer, 1952) but both techniques presently employed proved most of these oils to be excellent solvents of the polystyrene tested. One reason for the discrepancy may be reflected in differences in rates of solution. The beads produced by the precipitation technique for the ^{14}C study were much denser and had a much smaller surface area than the pre-expanded beads used in the observational technique. While the observational technique seldom took over 2 hr to achieve saturation of the solvent, the ^{14}C polystyrene did not attain a stable activity level for many hours of constant agitation. All of Boundy and Boyers (1952) compatibility observations were performed with extruded polystyrene, which has a desnity closer to the ^{14}C model. Extruded polystyrene also has a greater portion of the higher molecular weight polymer than does the expanded polystyrene (Wesphal, 1980). To study the effect that molecular weight might have on the solubiliby of polystyrene, citral and linalool were chosen for further investigation. Under two temperature conditions the molecular weight of the polystyrene tested had a marked effect on its solubility (Fig. 2 and 3). The direct relationship between temperature and solubility also helps explain the wide gap in solubility occurring in both these solvents in the observational tests at 20°C and 75°C.

All the terpenes tested proved to be excellent solvents for polystyrene. D-limonene, which comprises over 60% of most samples of pure lemon oil, was one of the best solvents tested. This could account for the decreased solubility of the higher quality oils (with various percentages of terpenes

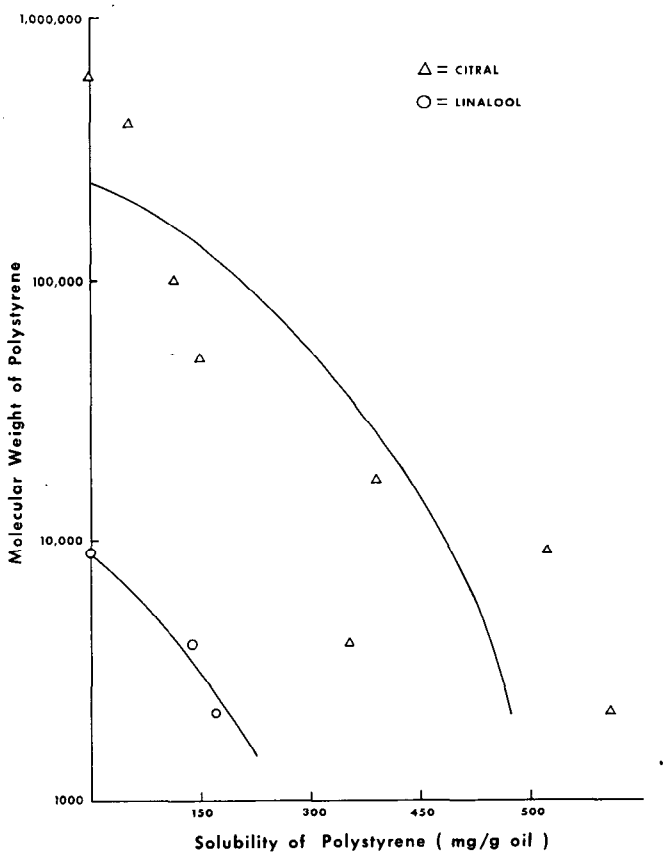

Fig. 2—Solubility of various molecular weight polystyrenes in citral and linalool at room temperature.

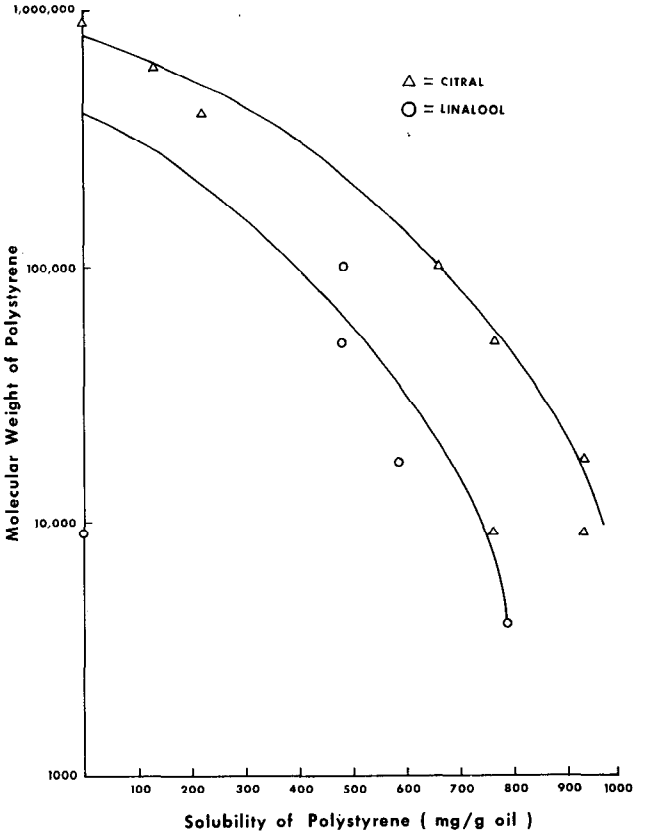

Fig. 3—Solubility of various molecular weight polystyrenes in citral and linalool at 75°C.

removed) and the very high solubility of terpenes. However, citral (an aldehyde) is also a major constituent of lemon and lemon grass oil and an important component of many widely used artificial food flavors. It showed good solvent potential, particularly at elevated temperatures.

All observed solubilities at 20°C were less than those determined by the ^{14}C method. The determination of saturation was highly subjective in the observational method and was difficult with the advent of significantly increased viscosity during the final stages of saturation of the better solvents.

The ramifications of the solubility of polystyrene in food depends on the interaction of these large solubilized molecules with food substances and the effect that they might have when ingested. The amount of polystyrene potentially found solubilized in foods must be put into perspective. Although some of the essential oils are far better solvents than the vegetable oils, they are also used in extremely low concentration when compared to the vegetable oils, which are foods. A recent study in this laboratory has shown that lemon oil in low concentrations, as in lemon tea, is actually absorbed by the polystyrene with which it makes contact. (Monte, 1982). This may account for the more rapid loss of certain flavor components from orange juice packaged on polystyrene as compared to glass (Durr et al., 1981). The fate of ingested solubilized polystyrene is currently being investigated, using a rat model, by one of the authors (W.C.M.).

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Kluyveromyces lactis (Anonymous, 1972). This suggests that the enzyme could be more useful in commercial processes than the yeast β-galactosidases. However, further work is needed to characterize the behavior of the enzyme in dairy systems, as opposed to the model systems reported in this paper.

Based on the information reported, additional work is being carried out to ascertain if the potential of *S. thermophilus* β-galactosidase can be put to use in a commercially viable process.

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